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RESEARCH ARTICLE

A GROWTH AND CHARACTERIZATION OF PURE AND GLYCINE DOPED KDP CRYSTALS BY GEL METHOD

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Abstract

Optically good quality pure and glycine doped KDP crystals have been grown by microbial free gel growth method at room temperature and their characterization of KDP crystals have been studied. The presence of functional groups of crystals are qualitatively analysed from FTIR spectra. X-ray diffraction study has been carried out in order to see the effect of dopant on the structural parameters of KDP. Thermal properties like decomposition temperature and weight loss have been reported from the TGA and DTA analysis. The transparency of grown crystals has been confirmed using UV-Vis-spectra. The second harmonic generation (SHG) was measured by using Kurtz powder technique. The relative second harmonic generation (SHG) efficiency of glycine doped crystals was higher than the pure KDP crystals. The dielectric behavior of pure and glycine doped crystals has been studied in the frequency range from 100Hz to 100 KHz.
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Keywords: Single crystal growth, growth from gel, non-linear optic, optical properties Dielectric studies

Introduction

Nowadays, the growth of technology is fast and high density data storage, data retrieving and transmission has demanded the search of new NLO materials with exceptional optical properties. NLO materials find application in high energy lasers for mertial confinement fusion research [1] electro-optic switches, colour display, frequency conversion [2]. Hence, there is vast demand to synthesis NLO materials and grow their single crystals because most of the physical, optical and electrical properties of the single crystals get deteriorated or completely diminished when there are not in the single domain crystal or having the defect like structural grain boundaries [3-4].

To grow the crystals having modified properties either by adding some functional groups [5] or incorporation of dopants [6,7] for tailor made applications. Potassium dihydrogen phosphate (KDP) is a known inorganic non-linear optical (NLO) material having unique ferroelectric, piezoelectric and elector-optic properties [8] KDP favors for its single crystal in large size therefore, its bulk size single crystals suitable for device fabrications have been easily grown by different techniques [9-11].

Generally amino acids have special features like chirality except glycine (asymmetric centre single carbon with four different groups) ie., non-centrosymmetirc crystallographic structure. The absence of strong conjugated bonds lead to the wide transparency ranges in the visible and UV-regions. The zwitter ionic nature of molecules, favour the stability of the molecules. In the present investigation, the effect of glycine doping in KDP crystals on structural SHG efficiency, optical transparency and thermal, dielectric properties have been investigated. The obtained results are discussed.

Experimental

Crystal growth

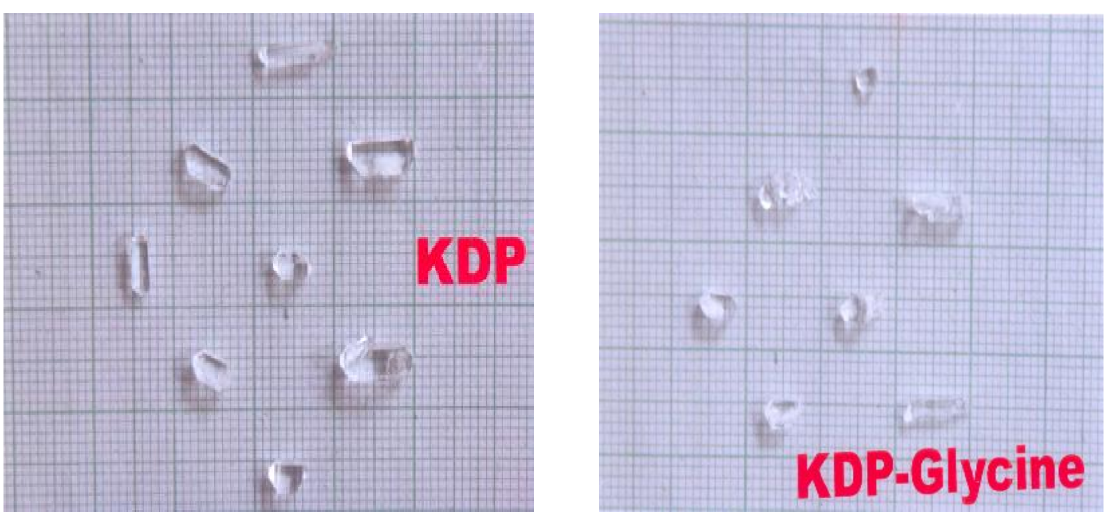
Pure and Glycine doped KDP single crystals are grown in sodium meta silicate gel medium using Analar grade KDP and glycine with concentration of 2.5M.

Pure KDP crystals were grown by using sodium meta silicate stock solution and KDP crystals. 10% Glycine doped KDP crystals were grown by same method. During the process pH was maintained at 4.5 at room temperature Fig (1).

Ethyl alcohol of equal volume is added over the set gel without damaging the gel surface. When the alcohol diffuses into the set gel, it reduces the solubility. This induces nucleation and the nuclei grown into the single crystals. The crystal growth was carried out at room temperature. The growth period was about 21 days for pure and glycine doped KDP crystals. Pure and KDP doped crystals are shown in the fig (2).

Figure. 1 Pure KDP and KDP-Glycine crystals growth near the interface and inside the gel

Figure. 2 Gel grown Pure KDP and KDP-Glycine crystals



Characterization

Fine powdered specimens of pure and glycine single crystals were subjected to Bruker D8 Advance powder X-ray diffractometer with nickel filtered CuK radiation (35Kv, 30ma) to see the effect of glycine doping on the crystal system and lattic parameters of grown crystals. The FT-IR spectra of pure and glycine doped KDP crystals were recorded using thermo-Nicolet Avatar 370 spectrophotometer in the range of 400-4000cm^{-1} with KBr pellet method of resolution 0.9cm^{-1}.Homogeneous powder was prepared and filtered through 120-125 microns test sieve and density filled in a micro-capillary of good quality glass of 1mm inner bore for. SHG measurements. The relative efficiency of pure and glycine doped KDP single crystals was measured by Kurtz and perry powder method [12] by using pure KDP as standard reference.

The optical transmission spectra were recorded for the pure as well as doped KDP single crystals in the wavelength range of 200-900nm using perkin Elmer lamba 35 UV-Vis. Spectrophotometer at ambient temperature. Vickers microhardness studies were carried out using Leitz-Wetzlar hardness tester equipped with a diamond square indenter. Different loads ranging from 25, 50 and 100 gm were used for these studies with a constant identification time of 10 sec. for all these crystals.

Results and Discussion

X-ray diffraction

Powder X-rd studies of pure and glycine doped KDP crystals grown by gel method confirmed the tetragonal structure of grown crystals. Results were compared with the JCPDS database where the prominent peaks of the reported values coincided with the investigated patterns. The crystals were identified by comparing the interplanar spacing and intensities of the X-rd pattern with the JCPDS data of KDP crystals.Pure KDP crystal belong to scalenohedral class of tetragonal system having the lattice parameters. a=b=7.488A^{O} and c=6.977A^{O} [13-14]. The slight shifts in the 2θ values of the doped crystals suggest that its structure was slightly disturbed compared to the pure KDP crystals Fig (3).

Optical properties studies

The recorded transmittance of pure and glycine doped KDP crystals in the wavelength 190-1100nm as shown in fig (4). It can be seen that the crystals have sufficient transmission in the entire visible and infrared region. The glycine doped KDP crystal grown by gel method has higher transmittance than pure crystal.

Thermal studies

TGA/DTA gives the idea about the thermal stability and decomposition of pure and glycine doped KDP crystals. TGA and DTA curve for pure and glycine doped KDP crystals have been recorded on Perkin Elmer Dimmer TG/DTA at a heating rate of 15^{0}C/mm under argon atmosphere the TGA of the samples indicate that they stable upto 200^{0}C atleast for all samples and weight loss is at temperature near 210^{0}C. It may be due to physically absorbed water. The weight loss in the temperature 250-350^{0}C is probably due to the decomposition of volatile substances and glycine. Fig (5).

It is found that three endothermic peaks at 210, 284, 317 for pure KDP and four peaks 204, 241, 284, 306 for glycine doped KDP crystals.The residual weight loss for pure KDP was 13.7% and for glycine doped 17.9%. This is due to the incorporation of glycine molecule into the KDP system. Glycine contains amino-acid group (NH_2CH_2COOH) and hence possibility of removal of ammonia ,water and carbondioxide (Volatile substance) more compared to pure KDP and hence the residual loss is higher than KDP.

Dielectric studies

Fig (6) shows the dielectric constant at different frequencies for the gel grown crystals of pure and glycine doped KDP crystals.

It is observed that the dielectric constant decreases with the increasing frequency upto 100 KHz. At higher frequencies the magnitude of dielectric constant depends on the degree of polarization and charge displacement in the crystals. The dielectric constant of materials is due to the concentration of electronic, ionic, dipolar and space charge polarizations which depend on the frequencies [15].

At low frequencies, all these polarization are active. The measured dielectric constant values are good agreement with reported results [16]. We observed that the glycine doped KDP crystals showed lower dielectric constant than pure KDP crystals.

Figure 3. Powder XRD pattern of Pure KDP and KDP-Glycine crystals

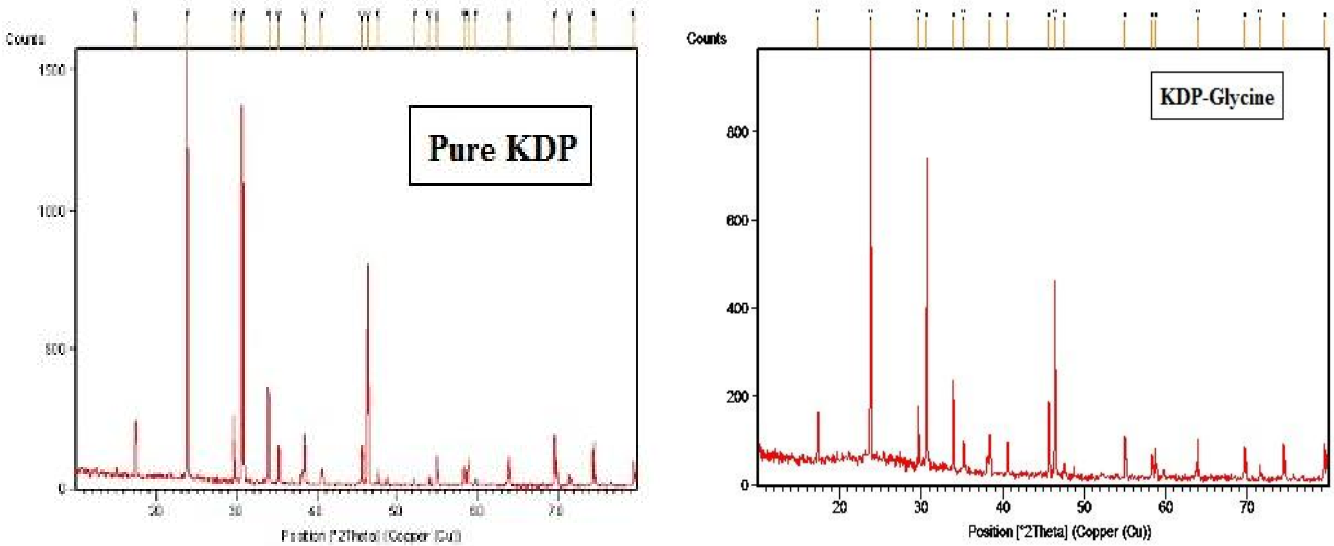


TABLE 1. Single X-rd lattice parameter

Sample	Lattice Parameter		~Z Z¥	Cell Volume V (A^0)	Structure
	a = b (A^0)	c (A^0)			
Pure KDP	7.466	6.986	90	389	Tetragonal
KDP-Glycine	7.429	6.933	90	382	Tetragonal

.

TABLE 2. The X-ray powder diffraction data for pure and glycine doped KDP crystals

Dt(1 wt % Pure KDP)	Dt (1wt% KDP-gly)	I (1wt% Pure KDP)	I (1 wt% KDP-gly)
5.1040	5.12140	Weak	Weak
3.7333	3.7403	Very strong	Very Strong
3.0107	3.0157	Weak	Weak
2.918	2.9168	Middle	Middle
2.6380	2.6425	Weak	Weak
2.5482	2.5525	Weak	Weak
2.3423	2.3461	Weak	Weak
2.2215	2.2245	Weak	Weak
1.9836	1.9853	Weak	Weak
1.9541	1.9563	Middle	Middle

The lower value of dielectric constant is a suitable parameter for the enhancement of SHG signals.

Michrohardness testing

The hardness of a material is a measure of its resistance to plastic deformation. The Vickers micro hardness number Hv was calculated by using relation.

$$Hv = \frac{1.8544\,P}{d^2}\ (Kg/mm^2)$$

P is the indenter load (Kg) and “d’ is the diagonal length of the impression (mm). The plots of Vickers hardness versus load for the gel grown pure and glycine doped KDP crystals is shown in fig (7) The glycine doped KDP crystals have Higher hardness with pure KDP. This is due to the incorporation of glycine amino acid.

FT-IR Analysis

The FTIR analysis of pure and glycine doped KDP crystals confirms the fundamental functional groups

Figure 4 . UV spectrum of Pure KDP and KDP-Glycine crystals

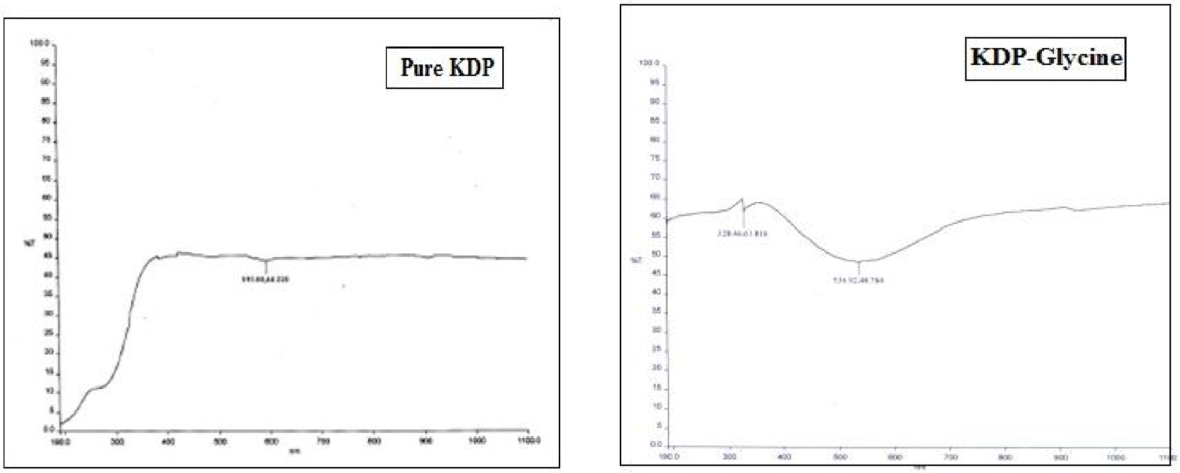


Figure 5. TG/DTA curve for Pure KDP and KDP-Glycine crystals

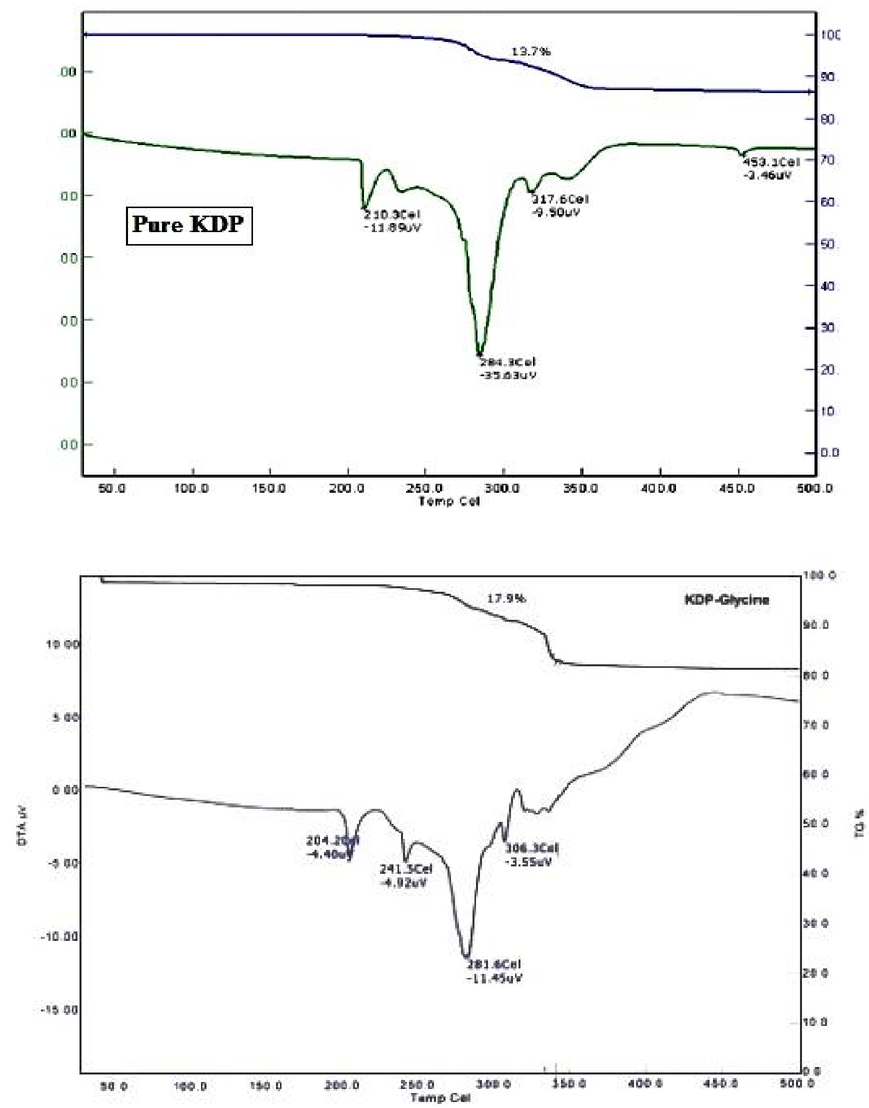


Fig.6 Dielectric constant for Pure KDP and KDP-Glycine crystals at room temperature

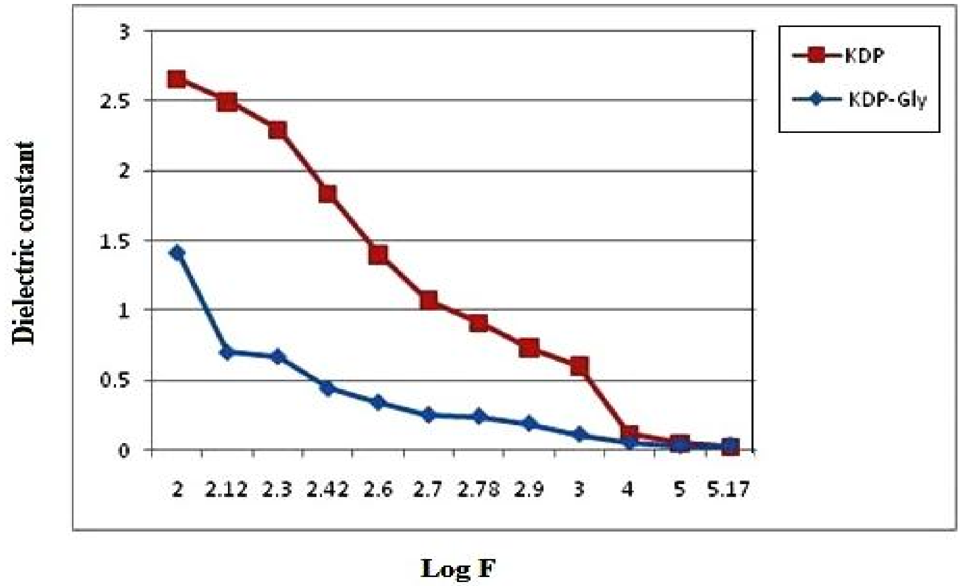


Fig.7 Vickers hardness of the grown Pure KDP and KDP-Glycine crystals

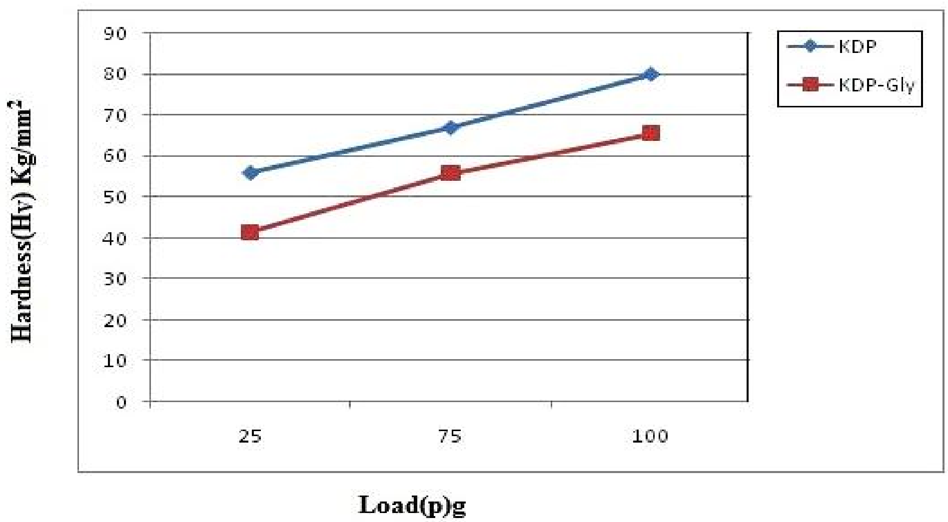


Table 3. Observed FT-IR frequencies and intensities of pure and Glycine doped KDP crystals

Calculated Value (cm^{-1}) Pure KDP	Pure KDP (cm^{-1})	KDP Gly (cm^{-1})	Assignement
3333	3446	3443	O-H Stret – Hydrogen bonded NH_3^+ asym. Street KDP
2358	2365	2364	P-O-H bending of KDP C=0 stretching
1650	1641	1641	Stretching of KDP NH_3^+ ant. Asy. Bending C=0 stretching
1390	1393	1400	CH_2 wagging
1290	1301	1302	PO- 0 stret of KDP
	1103	1102	P-O-H stret of KDP
904	897	899	N-H wagging
535	539	536	HO – P – OH bending Po_4 bending
450	450	455	N-H torsional oscillation

and the vibrational modes of KDP crystals. In the spectra of glycine doped crystals; some bands of $[H_2PO_4]$ overlap with glycine vibrations. The few bands of dihydrogen phosphate ion become broader and some of the frequencies are slightly shifted. The asymmetric stretching vibrations of NH_3^+ of glycine appear in the regions 3100 – 3450cm^{-1}. Some of them overlap with OH stretching vibrations of dihydrogen phosphate ion. The symmetric deformation NH_3^+, ion appears at around 1500cm^{-1} in the spectra of all doped crystals with medium intensity. The CH_2 bending vibrations of glycine appear around 1400cm^{-1}. These vibrations of glycine present in the spectra of doped crystals reveals the incorporation of impurities in the crystals fig (8).

SHG efficiency measurement

The gel grown crystals were carried out for the NLO study to measure the SHG efficiency of pure and glycine doped KDP crystals. To characterize the crystals, Kurtz and perry method was used.

The SHG efficiency of glycine doped KDP(8.0mJ) higher than pure KDP(7.8 mJ). This is due to the incorporation glycine amino acid into the pure KDP and made more polarization (NH_3^+ and COO^-) Zwitter ion made more polarization. This is very suitable for NLO applications.

SEM Studies

The surface morphology of grown crystals were confirmed by SEM images, where the growth conditions are unconstrained and the crystallites obtained are on the whole as seen in fig (9). Effect of glycine on the crystal morphology influence the volume of crystallites, the expanded capacity of crystallo graphic plane resulting in various crystallites.

Figure 8. FTIR spectra of Pure KDP and KDP-Glycine crystals

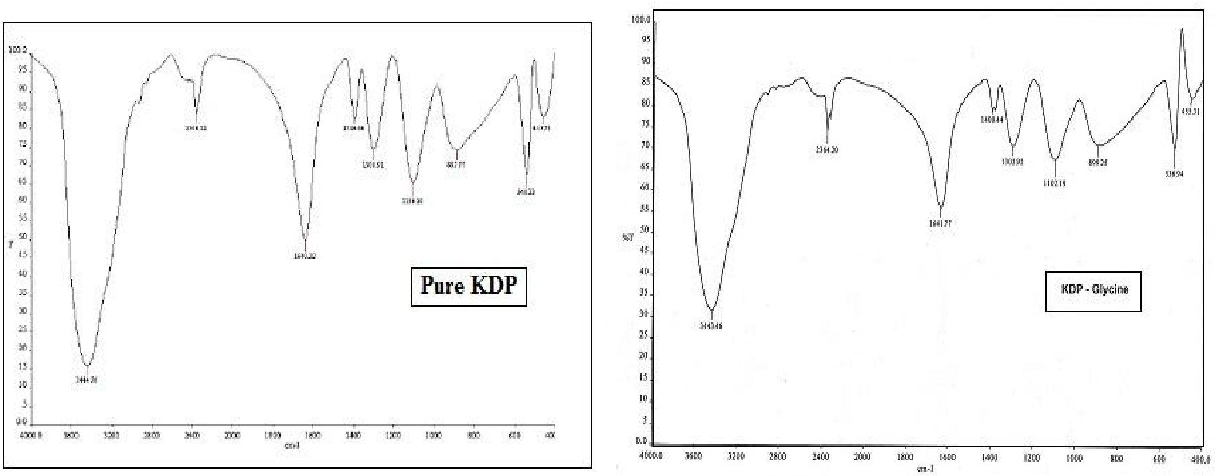
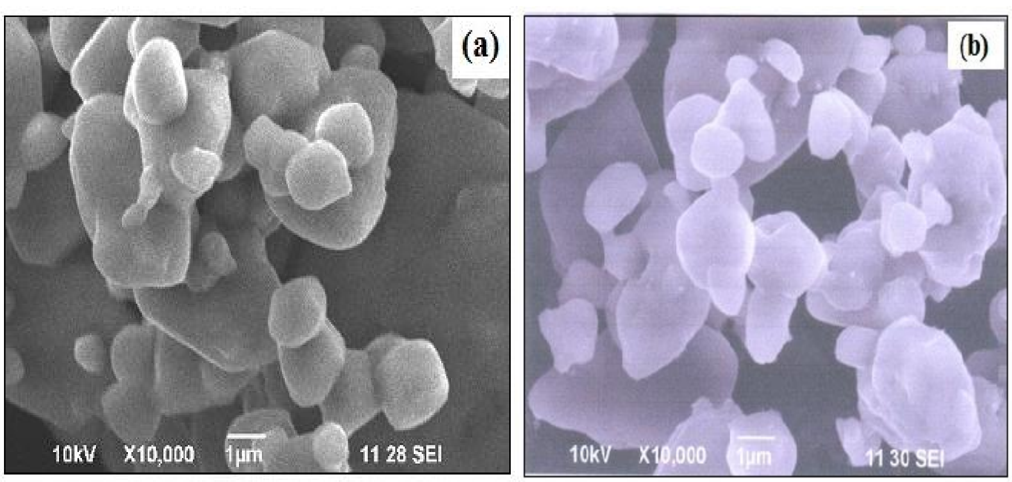


Figure 9. Surface morphology of Pure KDP and KDP-Glycine crystals



Conclusion

Good quality single crystals of pure as well as glycine doped KDP have been successfully grown by gel method. The gel grown crystals are free from microbes due to the three dimensional structure of gel formation. The powder X-ray diffraction analysis confirms the lattice dimension and crystal system of pure as well as doped crystals. No change was observed in the crystalline phase and tetragonal system but slight distortion in the lattice value due to the incorporation of glycine into the KDP crystal. The optical transmission analysis revealed that glycine doped KDP crystals have high percentage of transmission in the entire visible region, which is essential for NLO crystals. TG/DTA thermal studies revealed the stability and decomposition of grown crystals. Pure and glycine doped crystals are stable upto 200C.

The residual weight loss for pure KDP is 13.6% and for glycine doped was 77.0%. This is due to incorporation of glycine into the KDP lattice. The decomposition is due to liberation of carbon dioxide, water and ammonia.The lower values of dielectric constant on doping glycine was observed. The a.c. conductivity increases with frequency, obviously reverse trend was observed. For the a.c. resistivity the reduction in the values of a.c. conductivity on doping glycine is due to the basis of impurity presence in form of doping and the less defects. Low dielectric constant values indicate that the grown crystal contains minimum defects in gel growth.

Vicker microhardness measurements indicate the gel grown crystals have good crystalline perfection and low density defects, which is essential for various applications The FTIR studies confirms the presence of glycine in the doped crystals. The functional groups and various groups are confirmed by FT-IR frequencies compared with reported values.The SHG efficiency found to be increased for glycine doped comapared to pure KDP. This is due to the incorporation of glycine molecule into the KDP crystals and which make the crystal more polarizable. The SEM revealed the crystalline perfection and surface morphology of pure and glycine doped KDP crystals. The glycine doped crystals showed higher perfection.

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