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STUDY GROWTH AND CHARACTERIZATION OF CHLORIDE DOPED POTASSIUM DIHYDROGEN ORTHOPHOSPHATE CRYSTAL

S. Revathi*

*Department of Physics, Annai Women's College, Karur - 639 136, Tamil Nadu, India

ABSTRACT

Potassium dihydrogen phosphate (KDP) crystal has been doped with chloride to alter its physical and chemical properties.The pure and chloride mixtured KDP was grown by slow evaporation solution growth technique. The X-raydiffractometry (XRD) analys is shows that the crystalline perfection these optimum conditions is extremely good without having any internal structural grain boundaries and mosaic nature. The lattice parameters have been determined for pure KDP and chloride mixtured KDP from the single crystal XRD. The crystals grown by these optimum conditions show positive effects in the various characterization techniques.

Key words: KDP crystal, solution growth, XRD.

Corresponding Author E-mail: revathiadsaya@gmail.com

1. Introduction

Materials with large optical nonlinearity are needed to realize applications in optoelectronics, telecommunication industries, laser technology, and optical storage devices. ADP and KDP are two of the oldest crystals grown in large size for many applications and continue to be interesting materials both academically and industrially. Potassium dihydrogen phosphate (KDP) is an excellent inorganic nonlinear optical (NLO) material and has a considerable interest amongst several research workers because of its wide frequency, high efficiency of frequency conversion, and high damage threshold against high power laser. With the aim of improving the SHG efficiency of KDP, researchers have attempted to modify KDP crystals either by doping different type of impurities or by changing the growth conditions [1–9].

The adjustment effect of additives on the growth process and properties of crystals has been applied in recent years [10–12]. With additives, KDP crystals can be grown rapidly in the traditional crystallizers of simple design for conventional growth. In this present work, KDP crystals were grown from the aqueous solutions added with 1M % KCl and allowed to growth by optimum conditions.

2. Experimental Procedure

Pure KDP single crystal was grown by taking potassium dihydrogen phosphate and hydrochloric acid in 1:1 normality ratio. The calculated amount of potassium dihydrogen phosphate was taken in a beaker. The potassium dihydrogen salt was dissolved water. The calculated amount of hydrochloric acid is added slowly in the walls of the beaker containing aqueous solution of potassium dihydrogen phosphate. The resultant solution was stirred about 2 hours. The solution was heated about 40^{o}C . Finally the solution was filtered.

2.1 Growth Of Chloride Doped KDP Single Crystal

At first the solution was filtered to remove insoluble impurities. Then the supersaturated solution was covered by using a ordinary paper with perforations. Minimum number of holes were made (7-10) in the ordinary paper to control the evaporation. Then the solution was kept at room temperature in an undisturbed place for slow evaporation. After 4 days, the regular shaped crystal was harvested from the solution. The grown crystal as shown in Figure 1.

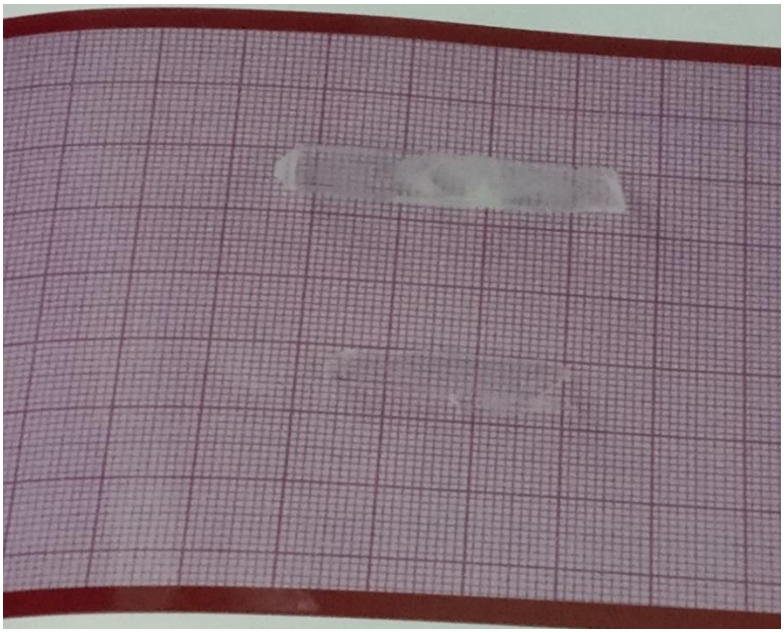

Fig. 1 Chloride doped KDP single crystal grown from slow evaporation method

3. Characterizations

The grown Sacrosine doped KDP crystals were subjected to various characterizations. Single crystal X-ray diffraction studies were carried out using single crystal diffractometer ENRAF NONIUS Cad4 and its lattice parameter volume structure and space group is analyzed in given in table. Powder X-ray diffraction studies were carried out using powder X-ray diffraction instrument D8 advanced BRUKER Spectrometer using CuKα radiation source and its wave length (λ=1.54Å), data collected from the 2θ range from 10°to 90° in steps of 0.020 and count time 0.2S. Identification of functional groups was carried out by FTIR analysis using JASCO 4100. UV-Visible spectral study is carried out using SHIMADZU 2600 in the range 200-1200nm. The flat surface of the LPKDP crystal were subjected to the hardness measurements using Leitz-Weitzlar hardness tester fitted with a Vicker's diamond indenter.

4. Results and Discussion

4.1 FTIR Analysis

The FTIR analysis of chloride doped KDP was carried out to investigate the presence of functional groups and their vibrational modes. The FTIR spectrum was recorded between the frequencies 400 and 4000 cm^{-1} using spectrum RXI spectrometer and the spectrum is shown in the Figure 2 and the assignment values are tabulated in table 1. The (OH) stretching mode is observed at 3780 cm^{-1}. The (OH) symmetric vibration mode is observed at 3417 cm^{-1}. The bands are observed at 2828 $cm^{-1,}$ and 2453cm^{-1} are due to contribution and overtones. The (P=O) asymmetric mode is observed at 1600 cm^{-1}. The (P=O) symmetric mode is observed at 1302 cm^{-1}. The (P-O) asymmetric mode is observed at 1094 cm^{-1}. The (P-O) symmetric mode is observed at 914 cm^{-1}.

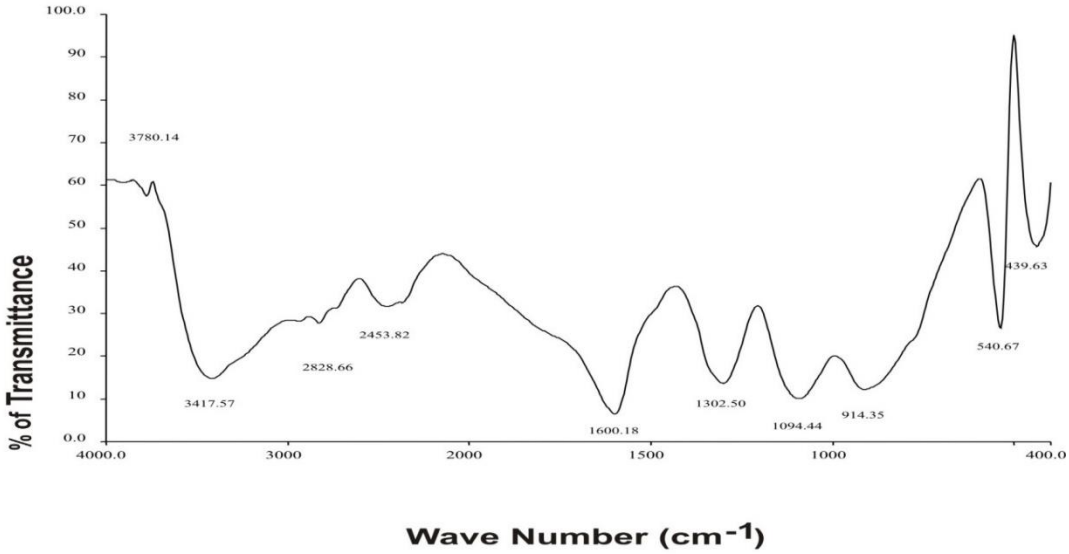

Fig. 2. FTIR spectrum of chloride doped KDP single crystal

The (O- P-O) stretching mode is observed at 540 cm^{-1}. The deformation mode is observed at 439 cm^{-1}[13].

4.2. UV- Vis –NIR Spectral Analysis

The optical transmittance spectra of chloride doped KDP single crystal was recorded in the range 190 -1100 nm using LAMBDA- 35 UV-VIS-NIR spectrometer. The Figure 3(a) shows that the UV-VIS –NIR spectrum of chloride doped KDP single crystal. The graph is drawn between transmittance against wavelength the cut off wavelengths are 320 nm for chloride doped KDP crystal grown from aqueous solution. It is clean from the transmittance spectrum that the crystal is well transparent throughout the entire visible region. The large transmission in the entire visible region enables it to be a good candidate for electronic devices.

Absorption spectrum

The optical absorption spectrum of chloride doped KDP single crystal was recorded in the range 190- 1100 nm using LAMBDA- 35 UV-VIS NIR spectrometer. The Figure 3(b) shows that the UV-VIS –NIR absorbance spectrum of chloride doped KDP single crystal.

From the absorbance spectrum, the cut off frequency is noted at 200 cm^{-1}. There is no absorbance throughout the entire region because the phosphate anions do not absorb radiation significantly in UV-VIS-NIR region [14].

Table 1 FTIR frequency assignment for HCl mixed KDP

Wave number	Tentative assignments
3780	(OH) stretching
3417	(OH) symmetric vibrations
2828	Combination bands
2453	Over tones
1600	(P =O) Asymmetric stretching
1302	(P =O) symmetric stretching
1094	(P -O) Asymmetric stretching
914	(P -O) symmetric stretching
540	(O-P-O) stretching
439	**(** P-OH) deformation

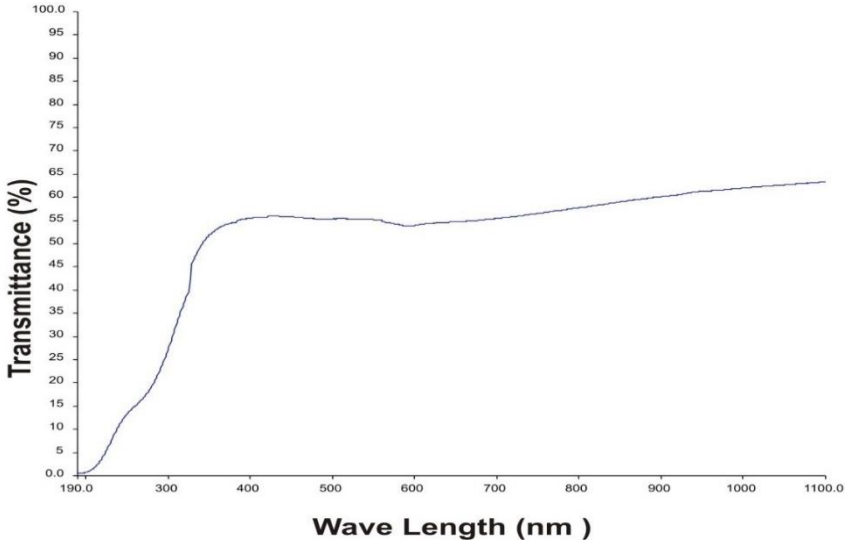

Fig. 3(a). UV-VIS -NIR Transmittance spectrum of chloride doped KDP single crystal

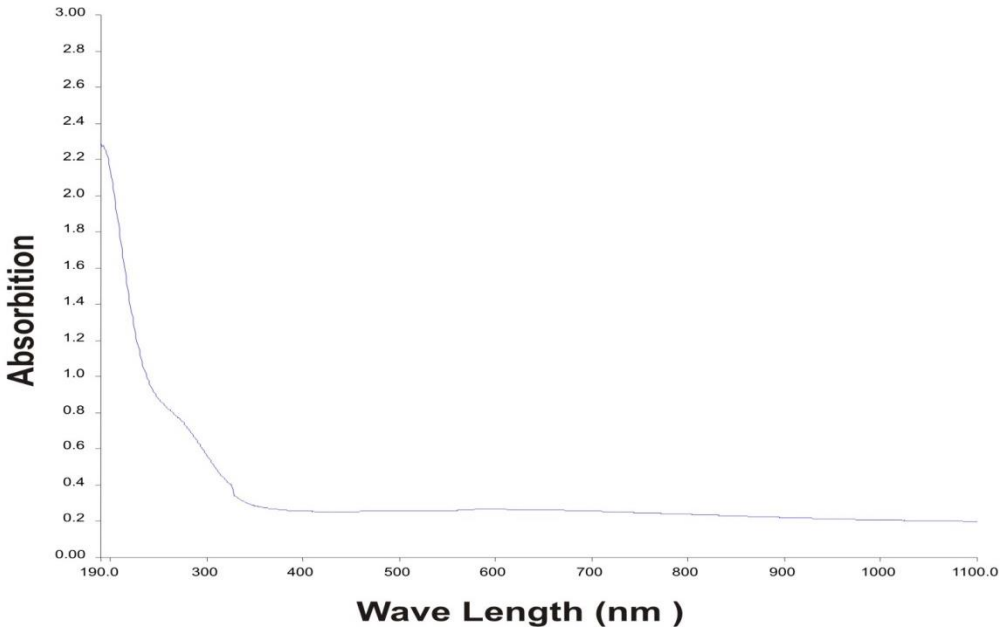

Fig. 3(b). UV-VIS -NIR Absorbition spectrum of chloride doped KDP single crystal

4.3 X-ray Single Crystal Analysis

Cell dimension of chloride doped KDP crystal

Single crystal X-ray diffraction study was carried out for chloride doped KDP single crystal using BRUKER- NONLUS CAD-4 diffract meter. Figure 4 shows that X-ray powder diffraction patterns for KDP crystals. Chloride doped KDP belongs to the Hexagonal crystal system. The cell parameters are

a = 6.316(1)A º, b = 10.531(5) A º,

c = 6.309(1) A º, α =90.00, β =113.02 º,

γ =90.00 º and Volume =386.2(2) A º 3

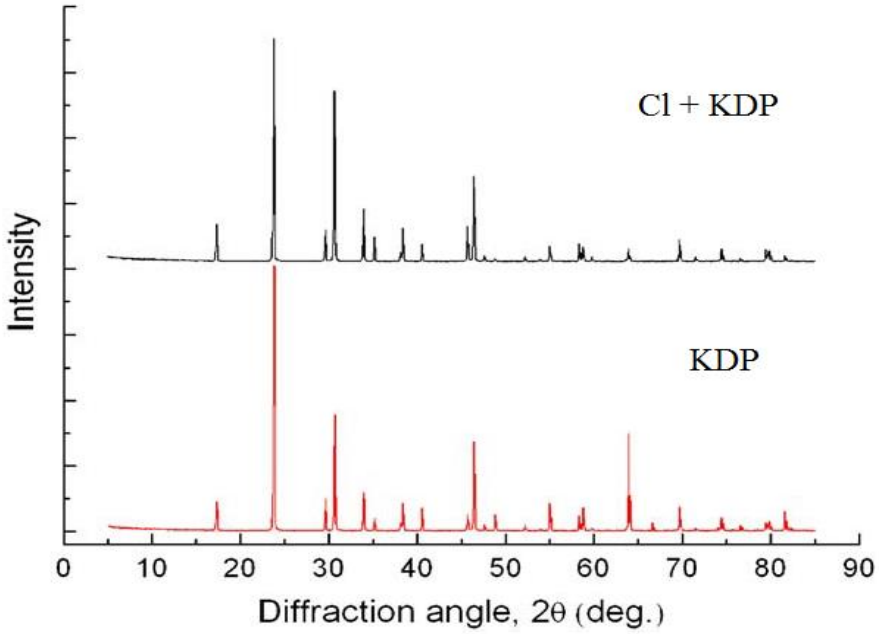

Fig. 4. X-ray powder diffraction patterns for KDP crystals.

4.4 Micro Hardness Studies

Micro hardness of a crystal is its capacity to resist indentation. Physically hardness is the resistance offered by a material to the localized deformations caused by scratching or by indentations. Micro hardness and anisotropy study using Vickers micro hardness is one of the important deciding factors in selecting the processing (cutting, grinding and polishing) steps for bulk crystals during the fabrication of devices. Interpretation of hardness is perceived as ability of a material to resist permanent deformation [15].

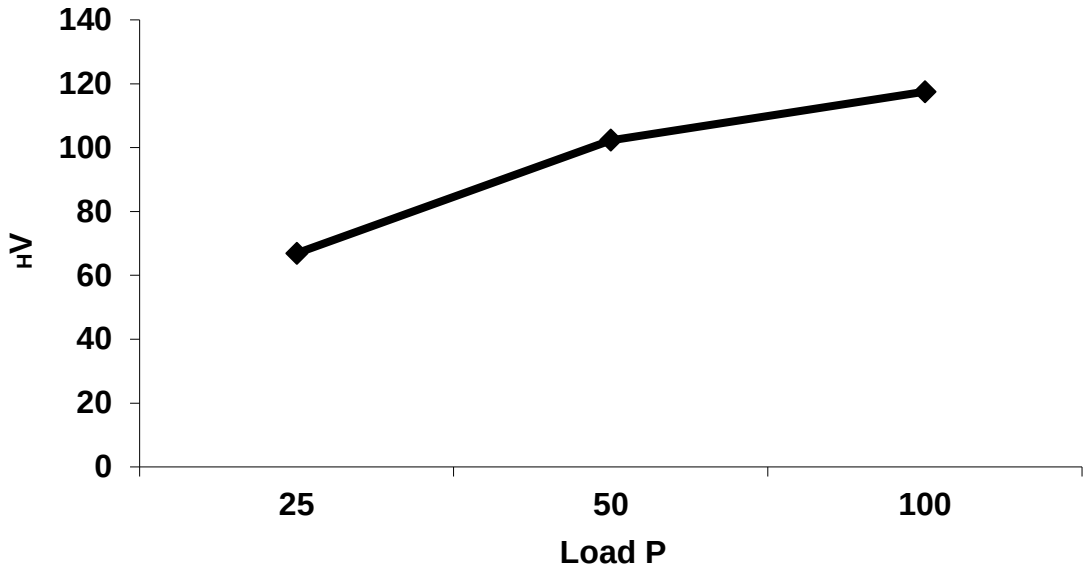

Fig. 5.1 Vickers Micro Hardness value Vs applied load for chloride doped KDP

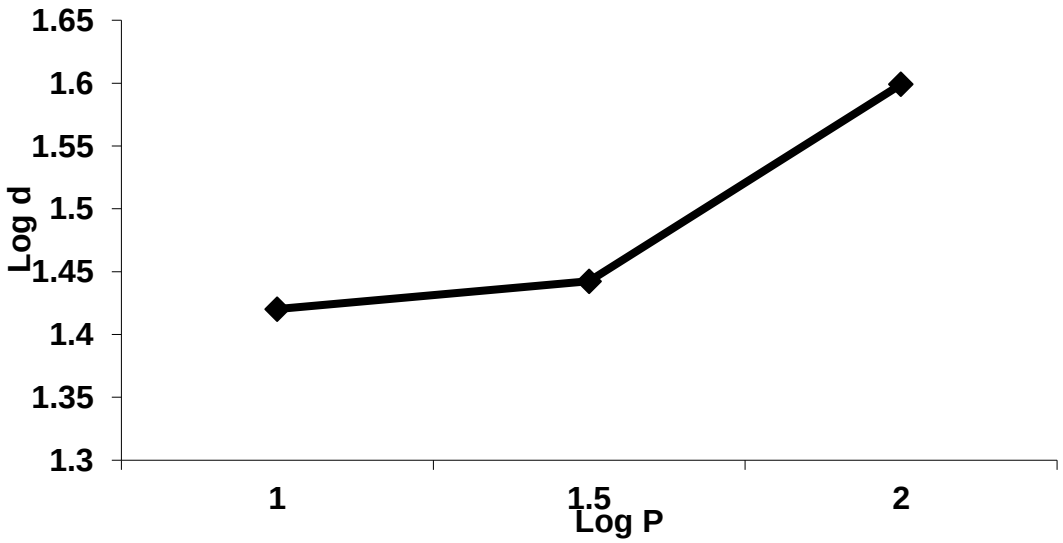

Fig.5.2 Log P Vs log d cure for chloride doped KDP single crystal

TABLE 2 MICRO HARDNESS OF CHLORIDE DOPED KDP SINGLE CRYSTALS

S.NO	Load (P)	Length (d)	Hv	Log (P)	Log (d)
1	25	26.3125	66.9	1.3979	1.4202
2	50	27.6925	102.3	1.6990	1.4424
3	100	39.725	117.5	2.0000	1.5991

Micro hardness measurement was carried out using square-based pyramidal diamond indenter having angle 136º between opposite faces. The hardness measurements were made on the prominent plane of the crystal of thickness 0.3mm using Leitz-Weizler Vicker's hardness tester fitted with a Vickers diamond pyramidal indenter and attached to an incident light microscope. Loads ranging from 25 to 100g were used for making indentations, keeping the time of indentation constant at 10s for all the cases.

The diagonal lengths of the indentation mark and crack length were measured, using the micrometer eyepiece at a magnification of X100.

$H_v = 1.8544(P/d^2)$ N/m^2

Where H_v is the Vickers hardness number, P is the applied load in kg/mm^2 and d is the average diagonal length of the impression observed in mm. Load Vs Hv curves are shown in figure 5.1.

The nonlinear behaviour of the micro hardness of the crystal differs from one plane to another which confirms the micro hardness anisotropy.

Initially the hardness value increases with increasing the applied load. log P Vs log d curves are plotted (figure 5.2).

The work hardening coefficient 'n' is calculated form the equation $F= a\ d^n$.

Here n is the Meyer's index (or) Work Harding co-efficient has been calculated from the slope of the straight line. The value of n is 2.6666.The calculated micro hardness values are presented in table 2.

Conclusion

The pure and chloride admixtured KDP was grown by slow evaporation solution growth technique . The lattice parameters have been determined for pure KDP and chloride admixtured KDP from the single crystal X-ray diffraction .The pure KDP belongs to tetragonal crystal system and chloride admixtured KDP belongs to hexagonal crystal system .Transparencies of these crystals were found using UV –VIS-NIR transmittance spectra and it has good transmittance window .The functional groups of these crystals were identified using Fourier Transform Infrared Spectra. The micro hardness studies performed on pure KDP and chloride admixtured KDP indicates that Vickers hardness number increases with increase of load.

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