INVESTIGATIONS ON DYES DOPED KDP CRYSTALS FOR POSSIBLE NON-LINEAR OPTICAL APPLICATIONS

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Abstract: ***The main aim of my research is to improve the NLO properties of KDP crystal by doping with organic impurities. KH_2PO_4 (KDP) crystal is widely used and thoroughly studied NLO crystals. The NLO and other properties of the crystal have been improved by doping of organic impurities. In the present investigation, Pure and dyes (Sudan I, Methyl Red and Evans blue) doped KDP crystals were grown by slow evaporation technique at room temperature. Grown crystals have been characterized using single crystal X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR), UV- visible spectroscopy and NLO studies. The presences of dyes were confirmed by FTIR and XRD spectra. Dye molecules possess π electron similar to conjugated polymers, but the molecules themselves are not very big. The analysis of single crystal XRD spectra conforms that all the doped samples have the perfect crystal properties. Their energy level structure shows the presence of bands containing many closely spaced levels corresponding to vibrational and rotational states. A variety of dyes for many laser operating wavelengths were employed in the past. The NLO reports of the samples are having high energy level comparing with pure KDP. Dyes embedded in KDP crystal and dye doped crystal were also reported as useful non-linear optical media.***

Key words: Crystal growth, KDP crystals, Dyes, FTIR Studies, NLO Studies.

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1. INTRODUCTION

Crystal growth is a controlled phase transformation to solid phase, either from solid or liquid or gaseous phase[1]. The growth units, namely the atoms or molecules, which diffuse to the growth site from the mother phase, when the given sufficient time to get orderly arranged on the lattice sites[2]. The search for new materials is primarily focused on increasing the non-linearity. With progress in crystal growth technology, materials having attractive non-linear properties are being discovered at rapid pace [3]. This has enabled the commercial development of single crystals with promising NLO properties.

KH_2PO_4 (KDP) crystal is widely used and thoroughly studied NLO crystals. The NLO and other properties of the crystal have been improved by doping of organic impurities. In the present investigation, pure and dyes (Sudan I, Methyl red and Evans blue) doped KDP crystals were grown by slow evaporation technique at room temperature[4-8]. Grown crystals have been characterized using single crystal X-ray diffraction and NLO studies. The presences of dyes were confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and UV- visible spectra.

2. EXPERIMENT

2.1 CRYSTAL GROWTH

Crystal growth techniques are generally classified in to three categories; they are growth from solution, growth from vapor and growth from melt. Each growth techniques has numerous variations, all materials cannot be grown by all the above three methods. In my present work the organic dyes such as Sudan I, Methyl red and Evans blue were doped with KDP in 0.1% ratio and grow by slow evaporation technique at room temperature[9].

Pure KDP crystals were grown from aqueous solution by slow evaporation and also by slow cooling method (0.5^0 C/Day). The same method is followed for doped KDP crystals (0.1 mole % of Sudan I). The solubility of doped KDP in the solvent was measured for each dopant, it was found to be 31.5-gms/100 ml at 42^oC for Methyl Red. The seed crystals are prepared at low temperature by spontaneous nucleation[10]. The seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystals of KDP and doped KDP were grown using constant temperature bath (CTB) controlled with an accuracy of 0.01^0C. The mother solution was saturated with the initial pH value, 4.2 for Evans Blue doped KDP crystal**.** The growth was carried out for more than 21 days by keeping the bath at a temperature of 39^0C.

2.2 SOLUBILITY

Growth from solution, in particular the low temperature solution growth, occupies an outstanding position due to its versatility and simplicity [11]. Growth from solution occurs close to equilibrium conditions and hence crystals of high perfection can be grown. Since the present research problem involves the growth of single crystals from low temperature solution, the processes of low temperature solution growth are briefly discussed [12].

It is desirable to study the solubility of the material in a suitable solvent before proceeding for the crystal growth. Solubility must be moderate and should have positive temperature gradient in a selected solvent[13-16]. Solubility of the pure and doped KDP in water was studied

gravimetrically. The water is mainly used as a natural solvent. If the compound is not dissolved in water then organic solvents such as acetone, ethanol, methanol etc are used. The dopent Sudan-I was not soluble in water. So we take acetone as solvent and mixed with KDP solution.

2.3 SLOW EVAPORATION TECHNIQUE

In this technique, an excess of a given solute is established by utilizing the difference between rates of evaporation of the solvent and the solute. A solution of the compound in a suitable solvent is prepared[17].

Unlike the cooling method, in which the total mass of the system remains constant, the solvent evaporation technique, the solution loses particles, which are weakly bound to other components and therefore the volume of the solution decreases. In almost all cases, the vapor pressure of the solvent above the solution is higher than the vapor pressure of the solute and therefore the solvent evaporates more rapidly and the solution becomes supersaturated (Petrov 1969). Usually, it is sufficient to allow the vapor formed above the solution to escape freely into the atmosphere. This is the oldest technique of crystal growth and technically, it is very simple.

The KDP salt was purified by repeated recrystallization using the method of dissolving in distilled water. Then the solution of KDP salt was prepared in a slightly under saturation condition[18]. The solution was stirred well for four hours constantly using magnetic stirrer still the salt has been dissolved in water. Then the prepared solution were transferred into two clean Petri dishes and kept for crystallization at room temperature in a quiet place. A supersaturated solution of pure KDP and 0.1% of Sudan I (dopent is separately dissolve in acetone and added with pure KDP solution), Methyl red and Evans blue doped KDP at room temperature was obtained by constant stirring up to five hours and then filter into beakers[19]. The good quality seeds were suspended in respective beakers using the nylon thread. Slow evaporation method was employed for the growth. After completion of growth run, the crystal was harvested. The photograph of grown pure KDP, Sudan I, Methyl red and Evans blue doped KDP crystal is shown in **figure 1(a),1(b),1(c) and 1(d).**

Figures 1(a),1(b),1(c) &1(d).Pure KDP and Dyes doped KDP Crystals

3. CHARACTERIZATION

3.1 Single X-ray diffraction studies:

The single crystal X-ray diffraction analysis has been carried out on the grown crystal. Single X-ray diffraction studies of pure and doped KDP crystals were carried out, using Bruker X8 Kappa ApeX11 XRD, X-ray diffractometer with Cu K_α (λ=1.54056Å) radiation[20]. The samples were scanned for 2θ values from 10˚ to 40˚ at a rate of 2˚ /min. Figure 2. Shows the unit cell determination of single crystal XRD pattern of the Pure, Sudan I, Methyl red and Evans blue doped KDP crystals.

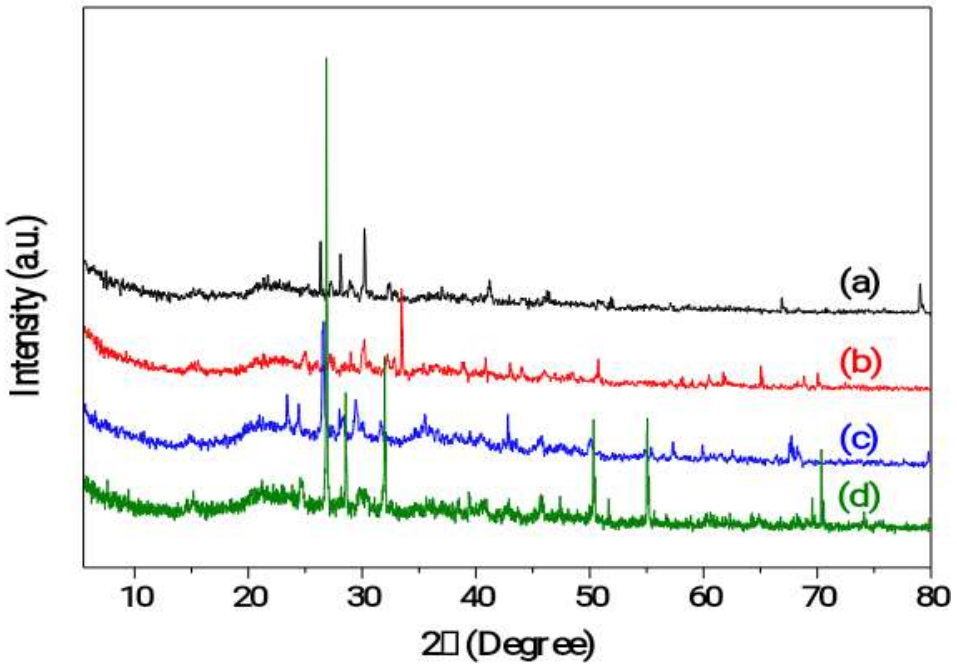

Figure2. XRD of (a) Pure KDP (b) Sudan I,(c)Methyl red and (d)Evans blue doped KDP Crystal

The diffraction patterns of the pure and dyes doped KDP have been indexed by least square fit method. It is seen that both the pure and doped crystals crystallizes variations in the lattice parameters which are due to the incorporation of the dopant in the KDP crystal lattice[21]. From this spectral analysis we conclude that the grown crystals all are having the crystals properties. This will show in table-1 the values of all doped samples having various crystal parameters (a, b, c) and the crystal system is tetragonal.

Table: 1 - Unit cell Determination

Samples	CRYSTAL SYSTEM	UNIT CELL PARAMETERS						
		a	b	c	α	β	γ	V
Pure KDP (KD01)	Tetragonal I	6.32	6.32	6.32	107.66	107.73	113	194
KDP + Sudan I (KP01)	Tetragonal I	6.34	6.34	6.35	112.88	108.19	109.83	195
KDP + Methyl Red (KP02)	Tetragonal I	6.35	6.36	6.35	113.37	107.77	107.38	197
KDP + Evans blue (KP03)	Tetragonal P	6.96	10.52	10.52	90.02	90.16	90.2	770

3.2. FTIR – Analysis:

The FTIR (Fig.3) of all of them were recorded from solid phase samples on a Perkin Elmer- Spectrum 2 FTIR/ATR model spectrophotometer consists of globar and mercury vapor lamp as sources, an interferometer chamber comprising of KBr and Mylar beam splitters followed by a sample chamber and detector. Entire region of 4000 – 450 cm^{-1} is covered by this instrument[22]. The instrument has a typical resolution of 0.5 cm^{-1}. Infrared spectrum is useful in identifying the functional groups like –OH, -CN, -CO, -CH, -NH2, etc. Also quantitative estimation is possible in certain cases for chemicals, pharmaceuticals, petroleum products, etc. The below figures show the graphical representation of the absorption spectrum of doped KDP samples. In the specified region of 530 cm-1 mostly all the samples having the maximum absorption ranges.

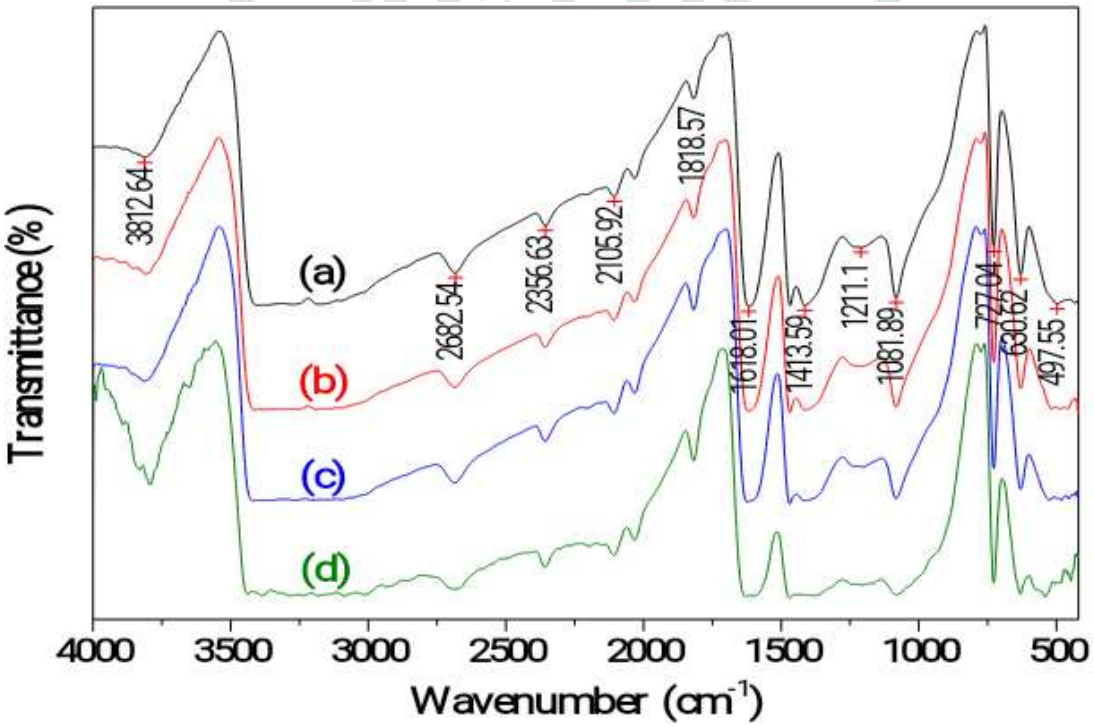

Figure 3. FTIR Spectra of (a) Pure KDP,(b) Sudan I,(c)Methyl red and (d) Evans blue doped KDP Crystal

3.3 UV – Visible Spectrum:

The UV – Visible spectroscopy of the pure KDP and doped KDP crystals was analysis done by UV – visible spectrophotometer model of Lambda 35 UV Winlab spectrometer. The scanning range of this instrument is 190 – 1100nm and also it can be used to study single crystals and powder samples.

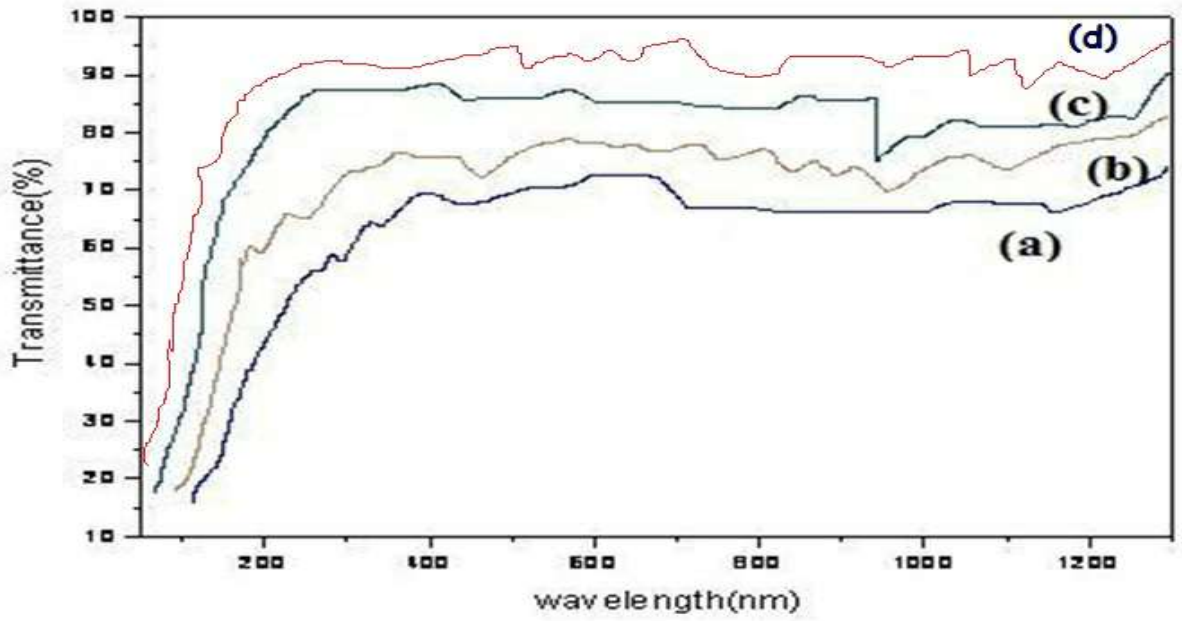

Figure 4. UV-Visible Spectra of (a)Pure KDP,(b) Sudan I,(c)Methyl red and (d) Evans blue doped KDP Crystal

This is a double beam instrument controlled by a microprocessor. The instrument has bandwidth range 0.5 – 4 nm (variable). The spectrometer is well suited for samples both in solid and the dissolved form. The absorption spectrums for samples were measured over the wavelength range 200 nm to 900 nm. The graphs for absorption have been plotted in Fig.4. The pure and doped KDP crystals show a good absorption between 200 nm to 900 nm.

3.4 NLO Analysis:

The NLO reports of the samples are having high energy level comparing with pure KDP. The above table – 2 shows variations and energy level difference in the pure and doped samples. Dyes embedded in KDP crystal and dye doped crystal were also reported as useful non-linear optical media[23].

Table : 2 – NLO Analysis

Sl. No.	Sample Code / Name of the Sample	Output Energy (milli joule)	Input Energy (joule)
1.	Sudan I doped KDP	12.98	0.70
2.	Methyl Red doped KDP	26.9	0.70
3.	Evans blue doped KDP	16.89	0.70
4.	Pure KDP	8.94	0.70

Specifications:

1. Q switched High Energy Nd:YAG Laser (QUANTA RAY Model LAB – 170 - 10)
Model HG-4B- High efficiency, angle tuned and temperature stabilized Second harmonic and Third harmonic Generator Crystals.Energy: 850 mJ, 450 mJ & 220 mJ:
Incident wavelength of the light: 1064 nm,
Wavelength of the light emitted from the sample: 532 nm
Repetition rate: 10 Hz (Pulse width: 6 ns)
2. Power & Energy Meter (Display Unit): (EPM 2000)
Sensor Head-Model: J-50-MB-YAG
Energy Range: 1.5 mJ to 3 J

4. RESULTS AND DISCUSSION

When Sudan I, Methyl red and Evans blue dyes has been doped with KDP crystal it has some changes in its characteristics. By comparing pure KDP crystal the characteristic analysis in dyes doped KDP crystal has been studied by using single crystal XRD and NLO analysis. The excitation of X-ray in KDP doped crystals has been found. While comparing the XRD pattern of doped KDP crystals with pure KDP crystal structure the 2 theta values slightly shifted towards left i.e. the 2 theta values decreased in fraction and hence the d-spacing range increased in fraction. The pyramidal plane (110) and (101) has been dominated heavily whereas the basal plane (200) is unaffected. From FTIR pattern it was found that a strong absorption peak near the wavelength of 480nm in pure KDP crystal. Whereas in Sudan I, Methyl red and Evans blue dyes doped KDP crystal the absorbance range is shifted towards the higher wavelength side around 480nm. This implies that Sudan I, Methyl red and

Evans blue dye finely incorporated in KDP crystal. The NLO reports of the samples are having high energy level comparing with pure KDP. Dyes embedded in KDP crystal and dye doped crystal were also reported as useful non-linear optical media.

5. CONCLUSION

Using FTIR and XRD analysis, the data Sudan I, Methyl red and Evans blue dyes doped KDP crystal has some changes in its structure. The shift of absorption and excellent transmission in entire visible region makes this crystal a good candidate for electronic applications. In the NLO report the samples are having high energy level comparing with pure KDP.The characteristics study of grown Sudan I, Methyl red and Evans blue dye doped KDP crystal indicated that this crystal can be a high NLO crystal than a pure KDP crystal.

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