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Mechanical and Dielectrical Properties of dyes doped KDP crystals for 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. KH2PO4 (KDP) crystal is widely used and thoroughly studied NLO crystals. The NLO and other properties of the crystal have been refined by doping of organic impurities. In the present investigation, Pure and dye Methyl Red 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 confirms 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 was also reported as useful non-linear optical media. The dielectric and mechanical properties of the materials are analyzed using LCRZ meter and Vicker's Microhardness Tester.

Keywords: *Crystal growth, KDP crystals, Dyes, FTIR Studies, NLO Studies, Dielectric studies .*

1. Introduction

Crystal growth is a controlled phase transformation to a 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 a rapid pace [3]. This has enabled the commercial development of single crystals with promising NLO properties.

The KDP crystal is extensively used and intensively studied NLO crystals. By doping the impurities like Methyl red the NLO and other properties of the crystal have been improved. In my present work, the pure and dye Methyl red doped KDP crystals were grown by slow evaporation technique at room temperature [4-8]. The well-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 into three categories; they are growing from solution, growth from vapour and growth from the melt. Each growth techniques has numerous dissimilarity, all materials cannot be grown by all the above three mentioned methods. In my present work, the organic dyes such as Methyl red 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 (0.50 C/Day). The same method is followed for doped KDP crystals. 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°C for Methyl Red. The seed crystals are prepared at low temperature by spontaneous nucleation [10]. Moreover, the seed crystals with ideal shape and free from macro defects were used for growth experiments. Large single crystals of KDP and doped KDP were grown using a constant temperature bath (CTB) controlled with an accuracy of 0.01°C. The mother solution was saturated with the initial pH value, 4.2 for Methyl Red doped KDP crystal. The growth was carried out for more than 21 days by keeping the bath at a temperature of 39°C.

2.2. Solubility

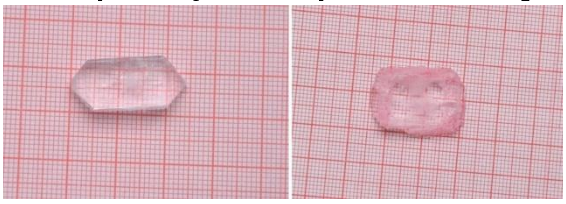
Growth from solution, in particular, the low-temperature solution growth, occupies an outstanding position due to its versatility and simplicity [11]. Growth from solution occurs close to equilibrium conditions and hence crystals of high perfection can be grown. Since the present research problem involves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

It is very important to study the solubility of the material in a suitable solvent before proceeding for the crystal growth. Solubility must be moderate and should have a positive temperature gradient in a selected solvent [13-16]. The solubility of the pure and doped KDP in water was studied gravimetrically. The natural solvent water is mainly used as a solvent. The compound is not dissolved in natural solvent then organic solvents such as acetone, ethanol, methanol etc are used.

2.3. Slow evaporation technique

In this technique, an excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and the solute. A solution of the compound in a suitable solvent is prepared [17]. Dissimilar the cooling method, in which the total mass of the system remains constant, the solvent evaporation technique, and the solution, loses particles, which are feebly bound to other components and therefore the volume of the solution decreases. In almost all instance, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and therefore the solvent evaporates more rapidly and the solution becomes supersaturated (Petrov 1969). Usually, it is adequate to allow the vapour formed above the solution to escape freely into the atmosphere. This is the earliest technique of crystal growth and technically, it is very modest.

The KDP material 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 was 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 Methyl red doped KDP at room temperature was obtained by constant stirring up to five hours and then filter into beakers [19]. The fine quality seeds were suspended in respective beakers. Slow evaporation method was employed for the growth. Then after the completion of growth run, the crystal was harvested. The photograph of grown pure KDP and Methyl red doped KDP crystal is shown in figure



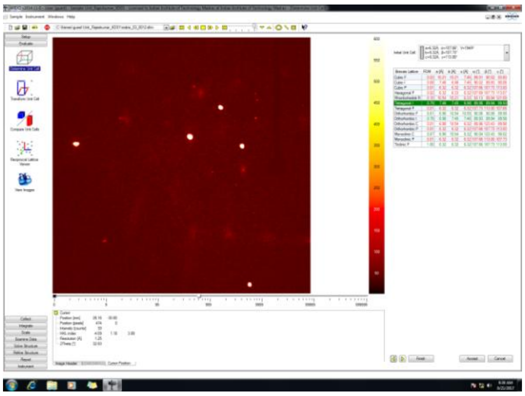
1(a) and 1(b).

Figures 1(a) and 1(b).Pure KDP and Dyes doped KDP Crystals

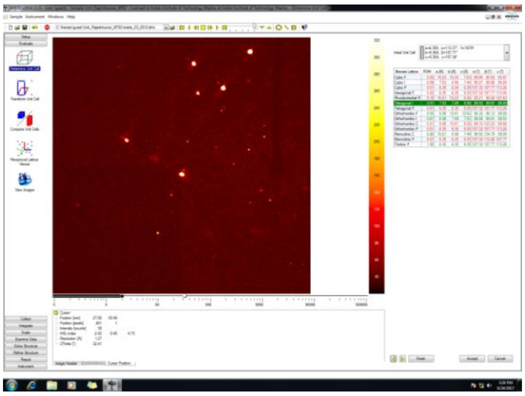
3. CHARACTERIZATION

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 Kα (λ=1.54056Å) radiation[20]. Here the pure and doped 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 and Methyl red doped KDP crystals. The diffraction The diffraction patterns of the pure and dyes doped KDP have been indexed by the least square fit method. It is seen that both the pure and doped crystals crystallize 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 properties of the crystals. 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.



(a)



(b)

Figure2. XRD of (a) Pure KDP (b) Methyl red and doped KDP Crystals.

Table: 1 – Unit cell Determination

MATERIALS	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 + Methyl Red (KP02)	Tetragonal I	6.35	6.36	6.35	113.37	107.77	107.38	197

3.2. FTIR – Analysis

The FTIR (Figure.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 vapour lamp as sources, an interferometer chamber comprising of KBr and Mylar beam splitters accompanied by a sample chamber and detector. An entire region of 4000 – 450 cm-1 is covered by this instrument [22]. The instrument has a typical resolution of 0.5 cm-1. The infrared spectrum is useful in identifying the functional groups like –OH, -CN, -CO, -CH, -NH2, etc. Also, quantitative estimation is conceivable in certain cases for chemicals, pharmaceuticals, petroleum products, etc. The graphical representation of the absorption spectrum of doped KDP samples is shown in figure-3. In the specified region of 530 cm-1 mostly all the samples having the maximum absorption ranges.

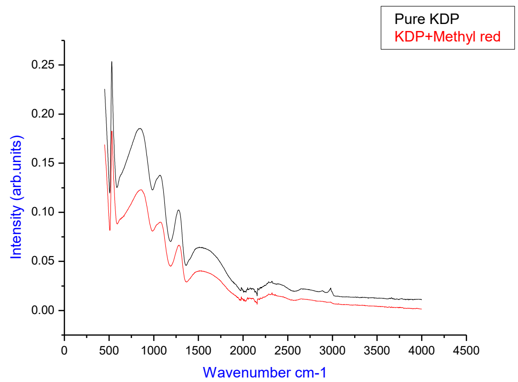


Figure 3. FTIR Spectra of (a) Pure KDP and (b) Methyl red doped KDP Crystals

3.3. UV – Visible Spectrum

The UV – Visible spectroscopy of the pure KDP and doped KDP crystals was an 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.

The microprocessor is used to control the double-beam instrument. 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 Figure.4. The pure and doped KDP crystals show a good absorption between 200 nm to 900 nm.

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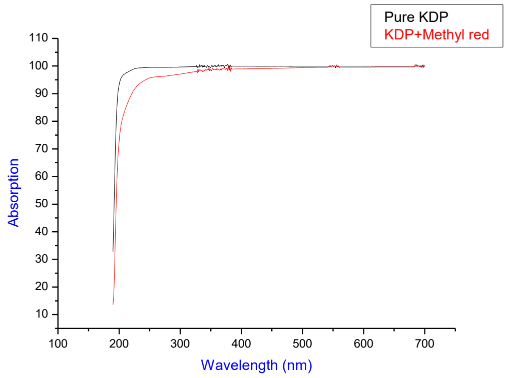

Figure 4. UV-Visible Spectra of (a)Pure KDP and (b) Methyl red doped KDP Crystals

3.4. NLO Analysis

The NLO reports of the samples are having high energy level comparing with pure KDP. The table – 2 shows variations and energy level difference in the pure and doped samples. Dyes embedded in KDP crystal and dye-doped crystals 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.	Pure KDP	8.94	0.70
2.	Methyl Red doped KDP	26.9	0.70

The specifications of an instrument are as follows, the 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. The energy was 850 mJ, 450 mJ & 220 mJ were used. The incident wavelength of the light is 1064 nm, a wavelength of the light emitted from the sample is 532 nm and the repetition rate is 10 Hz (Pulse width: 6 ns). The specification of Power & Energy Meter (Display Unit): (EPM 2000), and the Sensor Head-Model: J-50-MB-YAG. The energy range was used as 1.5 mJ to 3 J.

3.5. Microhardness Studies

Microhardness studies have been carried out on pure and doped KDP crystal using HMV SHIMADZU Vickers microhardness tester fitted with a Vickers diamond pyramidal indenter attached to an incident light microscope. Moreover, the static indentations were made at room temperature with a constant indentation time of 15 seconds for all indentations. The indentation marks were made on the polished faces of the sample by varying the load from 25 g to 100 g. beyond this load the formation of microcracks was observed, hence readings were not taken for higher loads. The Vickers microhardness was evaluated for the face (0 1 0) of the pure and doped KDP crystals. Vickers microhardness profile as a function of the applied test loads is illustrated in Figure.5. The decrease of the microhardness with the increasing load is compatibility with the normal indentation size effect (ISE). From the observations, we find that the creak length as follows. Left – 52.71, Right – 79.64, Up – 44.68, Down – 36.45

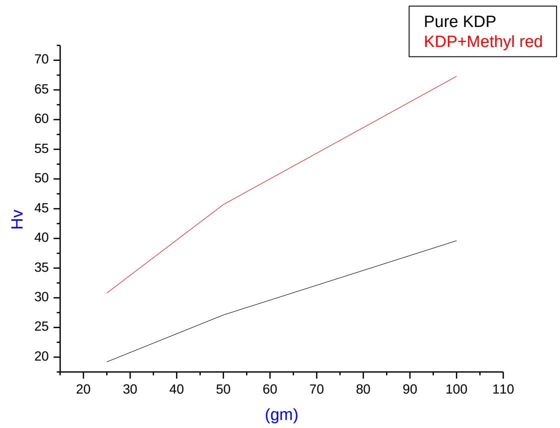

Figure.5. Variation of Hv with load for pure and Methyl red doped KDP crystal

3.6. Dielectric studies

The dielectric study was carried out using LCRZ Meter unit in the frequency range of 50 Hz - 200 KHz. Figure-10 shows the plots of the dielectric constant (εr) and dielectric loss (tanδ) versus

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frequency for pure and Methyl red doped KDP crystals. In the lower frequency region, the dielectric constant and dielectric loss have high values. The dielectric constant and dielectric loss both decrease as the frequency increases and at high-frequency region both remain almost constant, which is a normal dielectric behaviour [38-43]. The relation of the dielectric constant (εr) was calculated by

$$\varepsilon_r = [\ Cd / A\varepsilon_o]$$

Where C is the capacitance value of the crystal, A is the area of the crystal under investigation, d is the thickness of the sample used and εo is the permittivity of free space.

The loss tangent (tanδ) is a parameter of a dielectric material that quantifies its inherent dissipation of electromagnetic energy. The dielectric loss (ε”) was given by

$$\varepsilon'' = \tan\delta\ \varepsilon_r$$

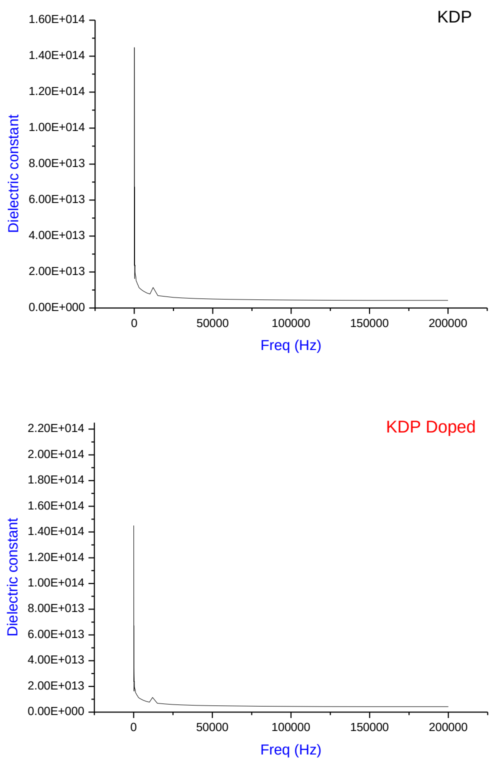
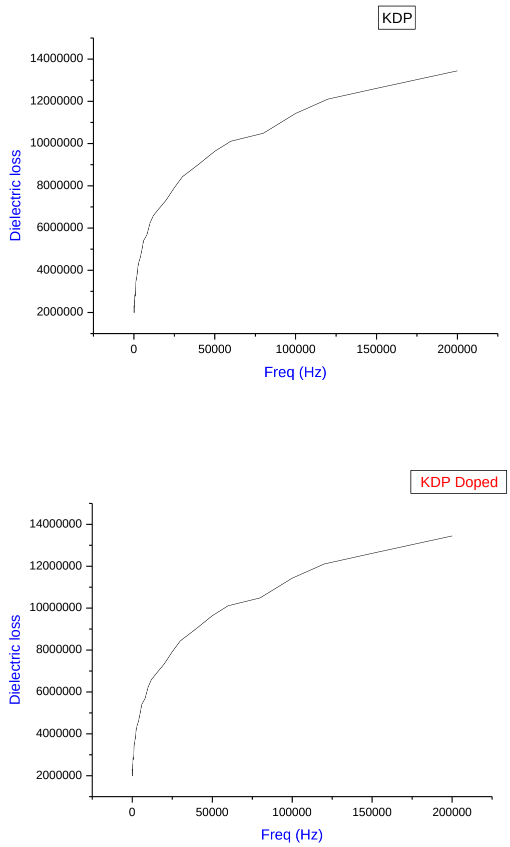


Figure 6. Dielectric constants for pure and doped KDP crystals



εr = [Cd / Aε

Figure 7.Dielectric losses for pure and doped KDP crystals

4. Results And Discussion

When Methyl red dye 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 the left i.e. the 2 theta values decreased infraction and hence the d-spacing range increased infraction. 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 Methyl red dye-doped KDP crystal the absorbance range is shifted towards the

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higher wavelength side around 480nm. This implies that Methyl red 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 crystals were also reported as useful non-linear optical media.

5. Conclusion

Using FTIR and XRD analysis, the data Methyl red dye-doped KDP crystal has some changes in its structure. The shift of absorption and excellent transmission in the 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 Methyl red dye-doped KDP crystal indicated that this crystal can be a high NLO crystal than a pure KDP crystal. It has a wide range of application in Non-linear optical media.

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