Growth, Optical and Stability Studies of Succinic Aacid Doped KDP NLO Crystal

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Abstract: ***Potassium dihydrogen phosphate, a well-known nonlinear optical material, has been grown with doping of succinic acid by a slow solvent evaporation technique. The crystals were undergone different characterizationlike X-ray diffraction and infrared spectroscopy analysis for confirmation. Optical transmittance and second harmonic generation efficiency were performed to determine its qualityforthe device. Its frequency conversion efficiency was found to be better than pure KDP. In order to find its mechanical and thermal stability, the crystal was subjected to microhardness testing and thermal analysis. EDAX analysis was done on this grown crystal to confirm the doping elements in KDP.***

Keywords: Crystal growth; Optical properties; X-ray diffraction; Nonlinear optical crystals; Thermal stability; Harmonic generators

PACS: 81.10; 78.66.Jg; 61.05.Cp; 42.70.Mp; 68.60.Dv; 42.65.Ky

1. Introduction

The overwhelming success of molecular engineering in controlling nonlinear optical (NLO) properties in the last decade has prompted better initiative in crystal engineering. Many of the materials used for photonics are NLO materials, which mean that they interact with light in such a way that the light changes the properties of the material, which, in turn, changes the properties of the light. One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Potassium dihydrogen phosphate (KDP) is a model system for nonlinear optical device application; it continues to be an interesting material both academically and industrially and is extensively studied from various aspects. Its excellent qualities such as high nonlinear conversion efficiency, wide optical transmission range with low cutoff wavelength have drawn the attention of several crystal growers. The new materials inspected for nonlinear optical applications had always been inorganic. Many inorganic crystals are well examined in terms of their physical properties. These materials are mostly ionic bonded, and it is easier to synthesize. Inorganic materials often have a high melting point and a high degree of chemical inertness. The NLO coefficient of KDP crystal is low comparing organic materials. Efforts are being taken by scientists all over the world to increase its NLO efficiency by introducing elements as substitutional and interstitial dopants. Many reports on the enhancement of the properties have come out based on the dopants. Improvement in the quality of KDP crystals and the performance of KDP based devices can be realized with suitable dopants [1-3]. In view of developing the second harmonic generation efficiency of KDP crystal, an attempt was made to incorporating succinic acid, one of the dicarboxylic acid groups, and revealing its properties to meet the requirements of the NLO device.

2. Crystal Growth

A homogeneous aqueous solution of potassium dihydrogen phosphate (KDP) was prepared in a glass beaker at 35 ℃ by continuous stirring of the solution about 5 hours. The process of stirring was done until it attains saturated condition. The pH value of the solution was noted as 5 using electronic digital pH meter. Then the prepared solution was filtered by whatmann filtered paper in a well cleaned glass beaker and made it for slow evaporation at room temperature. The beaker was closed by a polythene cover with some perforated holes and kept on a stable in a dark place. After 5 days a small nucleation was observed at the bottom of the beaker. It was allowed to grow for a fortnight to become a bulk size to be required for optical testing. Then the crystals were harvested from the mother solution. They were placed on a graph paper for measuring the dimension of the crystal. The dimension of the crystal harvested is 16x10x4 mm^3, which is shown in the Fig. 1(a). In order to grow succinic acid doped KDP crystal and compare the physical properties, 1 mol % of succinic acid (1.18 g) was added into the 1 molar mass of KDP (136.084) substance and then its solution was prepared homogeneously by adding distilled water and stirred it about 6 hours at 35℃. The pH value of the solution was measured as 4, which is

International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2020): 7.803

due to the addition of succinic acid. After the filtration, the solution was made to open evaporation at ambient temperature and hence a small nucleation could find in 2 days after at the bottom of the beaker. One week later an adequate size crystal of dimension 32x28x6 mm^3 was harvested, which is shown in the Fig. 1(b).

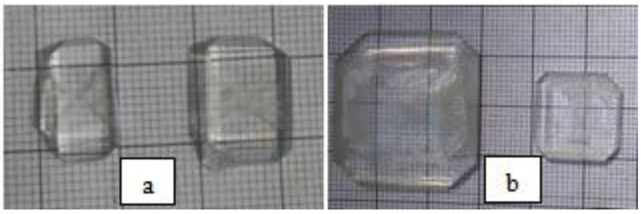

Figure 1: (a) Photograph of pure (b) 1 mol % of succinic acid doped KDP crystal

3. Experimental Methods

Succinic acid doped KDP crystal was subjected to different characterization to reveal its properties and to be utilized for a nonlinear optical device. From research to production and engineering, X-ray diffraction XRD is an indispensable method for materials characterization and quality control. Hence, X-rays are used for the investigation of the single crystal to determine its crystal structure and space group. The grown crystalline structure was determined by both single crystal and powder X-ray diffraction, and their result was compared with the reported cell parameter. Single crystal X-ray diffraction analysis was performed by a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite monochromated Mo (Kα) radiation of wavelength 0.7107 Å. Powder X-ray diffraction (PXRD) of the grown crystal was recorded using Seifert Dyz 2002 model powder X-ray diffractometer with CuKα radiation of wavelength λ = 1.540598 Å. FTIR is perhaps the most powerful tool for identifying the types of chemical bonds (functional groups). In order to analyze the presence of functional groups in the succinic acid doped KDP crystals qualitatively, Fourier transforms infrared spectrum was recorded between 4000 and 450 cm^{-1} using Perkin-Elmer spectrum one FTIR spectrometer. The optical transmittance range and transparency cutoff wavelength are the main requirements for device applications. The measurement of the band gap of materials is important in the semiconductor, and solar industries. This note demonstrates how the band gap of a material can be determined from its UV absorption spectrum. The UV-Vis-NIR transmission spectrum of good quality 1 mol% succinic acid doped KDP single crystal grown in the aqueous solution was recorded in the range 200 to 1100 nm using Perkin Elmer Lamda 35 UV/VIS spectrometer.

Materials, which can generate the second harmonic frequency, play an important role in the domain of optoelectronics and photonics. Crystals possessing for nonlinear optical properties with high conversion efficiencies for a second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for several device applications. The second harmonic generation (SHG) is used as a tool to evaluate qualitatively the bulk homogeneity of the samples under investigation [4]. It is a relevant technique for frequency conversion effect in a laser device. The SHG behavior of powdered succinic acid doped KDP sample of particle size 150 micron, which was prepared by a sieve with the same size of mesh, was analyzed using Kurtz-Perry powder technique. Thereafter it was compared with the standard pure KDP crystal in powder form with the same range of size. A high intense Nd: YAG laser source was used whose beam wavelength and energy is 1064 nm and16.5 mJ/pulse respectively. The corresponding input pulse and a pulse-width is 1mV/pulse and 10 ns. The laser radiation was allowed to pass through the sample taken in the form of powder in a microcapillary tube. Pure KDP was used as a reference sample. Both the reference and test samples had a uniform particle size of 150 microns. The experiment was carried out in pure KDP and later in the succinic acid doped KDP sample. The mechanical strength of the materials plays a key role in device fabrication. It is a measure of the resistance; the lattice offers to local deformation. Selected smooth and flat surface of the grown crystal was subjected to hardness studies at room temperature with the load ranging from 25–200 g using Vickers's hardness tester fitted with a diamond pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5 s for all the loads.

The term "thermal analysis" refers to a group of techniques in which some physical or chemical property of a system is measured as a function of temperature. All materials, as they experience changes in temperatures, undergo changes in their physical and chemical properties. These changes can be detected by suitable transducers that convert the changes into electrical signals, which are collected and analyzed to give thermograms showing the property change as a function of temperature. Thermal properties melting point and dissociation temperature of succinic acid doped KDP single crystal were studied by Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). These were carried out between 30 °C and 900 °Cin nitrogen atmosphere at a heating rate of 10 °C/min using SDT Q600 V20.9 Build 20 TG/DTA instrument by stepwise isothermal method. Analytical Energy dispersive X-ray analysis (EDAX) is a micro-technique that uses the characteristics spectrum of X-rays emitted by the sample after excitation by high energy electrons. This analysis is used to obtain information about the elemental composition of the grown crystals particularly to determine the dopant. The elemental analysis has been carried out by employing the energy dispersive X-ray analysis (EDAX) technique using the Jeol6390LV model scanning electron microscope instrument. The energy spectrum of the succinic acid doped potassium dihydrogenphosphate single crystal has been recorded in the range of 0–10 keV.

4. Results and Discussions

The title compound succinic acid doped potassium dihydrogen phosphate crystallizes tetragonal structure with the noncentrosymmetric space group of $I\bar{4}2d$. The unit cell parameters determined by the single crystal X-ray diffraction method are a=7.411(1) Å, c= 6.948(3) Å,and volume of the unit cell is V= 381.604 $Å^3$. The powder XRD pattern of the grown crystal is shown in the Fig.2, in which the crystallographic plane was identified using two thetasoftware.

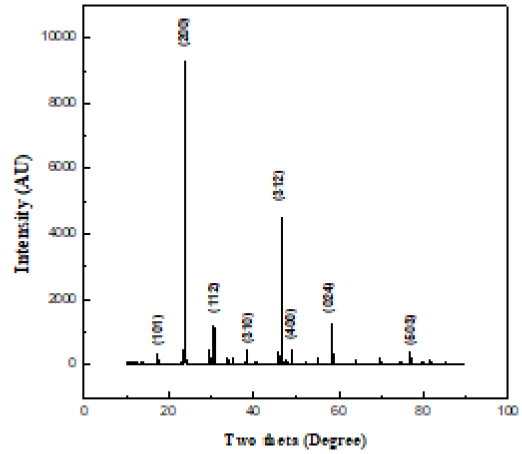

Figure 2: Powder XRD pattern of succinic acid doped KDP crystal

The peak of the powder XRD pattern indicates the crystalline nature is good.The crystallographicparametersand its diffraction pattern were compared with the literature values [5, 6] and they are highly agreed with them. The Fourier transform infrared spectrum of succinic acid doped KDP is shown in the Fig.3. Generally, the hydroxyl group has broadband at a higher energy of vibration from 2400 to 3500 cm^{-1}. In this spectrum, the stretching vibration between 2429 and 3318 cm^{-1} is corresponding to the characteristics of OH vibration. The frequency at 3318 and 3265 cm^{-1} is assigned for OH stretching vibration. In P-OHgroup, a strong stretchingvibration takes place at 2748 cm^{-1}, which is due to

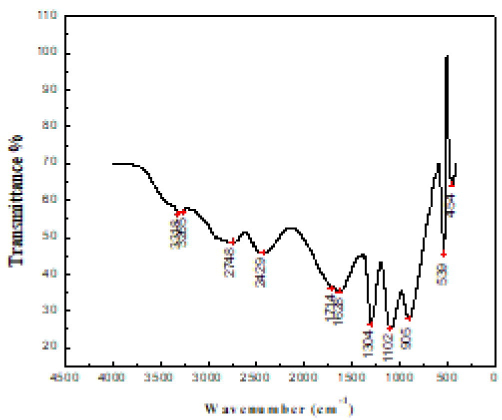

Figure 3: FTIR Spectrum of Succinic acid doped KDP crystal

the vibration of OH vibration and the frequency at 2429 cm^{-1} is due to the PH vibration. The potassium hydrogen KH stretching vibration takes place at 1628 cm^{-1}. There is a strong stretching vibration obtained at 1304 cm^{-1}, which is due to P=O stretching vibration. The very strong stretching vibration for phosphate ion PO_4^{3-} is assigned at 1102 and its bending band is observed at 454 cm^{-1}. The KO stretching and PO bending band occurs at 905 and 539cm^{-1} respectively. The frequency of all fundamental vibrations of the functional groups in the compound succinic acid doped potassium dihydrogen phosphate is given in Table 1.

The transmittance spectrum of the grown crystal is shown in the Fig.4, in which the lower cut off

Table 1: Frequencies of the fundamental vibrations of succinic acid doped KDP crystal

Frequency in wavenumber (cm^{-1})	Assignment of vibrations [7-9]
3318	OH stretching
3265	OH stretching
2748	OH stretching of P-OH group
2429	PH stretching of P-OH group
1714	KH stretching
1628	KH stretching
1304	P=O stretching
1102	PO_4^{3-} strong stretching band
905	KO stretching
539	P-O bending band
454	PO_4^{3-} bending band

region for both pure and doped KDP sample is obtained at 250 nm. There is a very good transmittance from 350 to 1100 nm wavelength found in pure and doped crystals. It is observed that the lower cut off wavelength is 250 nm for both the crystals and transmittance is more than 90 % in the visible region and 95% in the near infrared spectral region for pure KDP. The maximum transmittance is 96 % in thenear infrared region. But in the spectrum of this doped

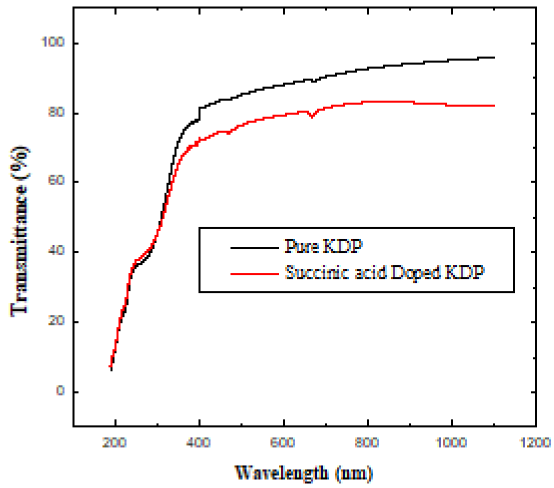

Figure 4: Transmittance spectrum of Pure and succinic acid doped KDP

KDP crystal, the transmittance range is 80%, which is a little lower when compared to pure KDP crystal. This is due to more absorption of the dopant material. Here it is observed that there is a steady transmittance in both visible and near infrared region. Fig.5 shows the optical absorbance of the pure and doped KDP crystal. In both thespectrum there is no remarkable change found in the visible region.Optical band gapwas

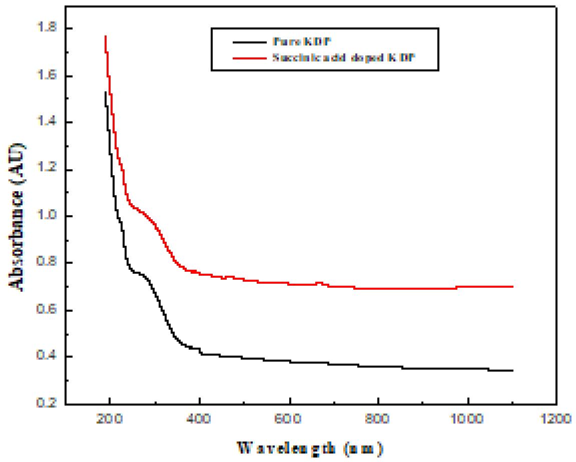

Figure 5: Optical absorbance spectrum of Pure and succinic acid doped KDP crystal

found to be 5.6 eV by extrapolating the curve in the Fig.6 drawn between $(\alpha h\upsilon)^2$ and photon energy hυ, to the x-axis. Thesuccinic acid doped KDP sample, packed in a microcapillary tube in the form of very fine powder, was placed in the path of Nd-YAG laser beam. The beam voltage of the transmitted radiation was 24 mV when pure KDP crystalline sample in the form of powder was used as reference material. But the transmitted beam voltage through the succinic acid doped KDP sample was measured as 30 mV. Hence the SHG efficiency is 1.25 times greater than that of the standard KDP crystal. The transmitted beam from the sample holder was observed in green color and the wavelength of the beam was 532 nm. From the observation and measurement made on the beam voltage and compared with the standard NLO material pure potassium dihydrogen phosphate, it is a good candidate for the conversion of frequency in a nonlinear optical device.

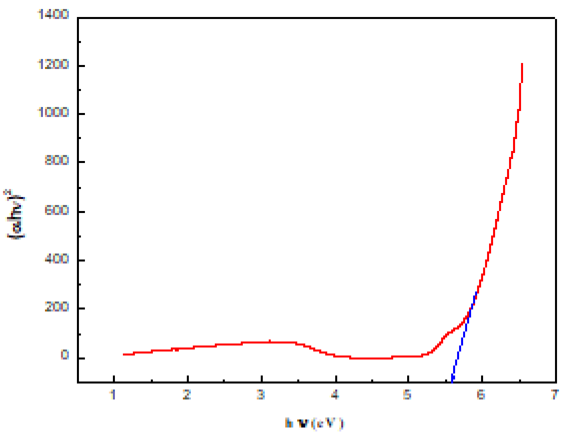

Figure 6: Plot of $(\alpha h\upsilon)^2$ v_s. photon energy of succinic acid doped KDP crystal

In order to find the mechanical properties of the grown crystal for nonlinear optical device applications, the grown succinic acid doped KDP crystal was subjected to a various load in the step of 25 g and measured indentation length. They were analyzed using HMV2T Vicker's Microhardness tester. The Vicker's microhardness values were calculated from the standard formula $H_v = 1.8544\ P/d^2$ kg/mm^2, where P is the applied load and d is the mean diagonal length of the indentation. A graph (Fig. 7) was drawn between the applied load and calculated hardnessvalue and it is observed that there is an increase of hardness with the increase of load up to 200 gram and crack forms on the crystal when 200 g load is applied. The maximum crack length developed on the crystal was measured as 81.88 µm from the center of the indentation. The microhardness value was calculated using the formula for various load and the corresponding diagonal length of the indentation formed on the crystal.

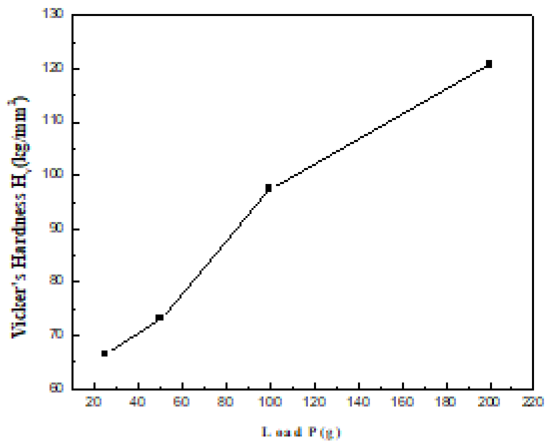

Figure 7: Hardness Vs load graph of Succinic acid doped KDP crystal

The maximum hardness obtained in this material is 120.69 kg/mm^2. In order to find work hardening coefficient (n) of the grown crystal, a graph (Fig.8) was drawn between logarithmic values of load and a diagonal length of indentation. Using Meyer's law ($P = ad^n$) connecting the relationship between applied load and adiagonal length of the indentation, it was calculated as 2.32. Here, "a" is the constant for the given material. According to Onitsch,if n lies

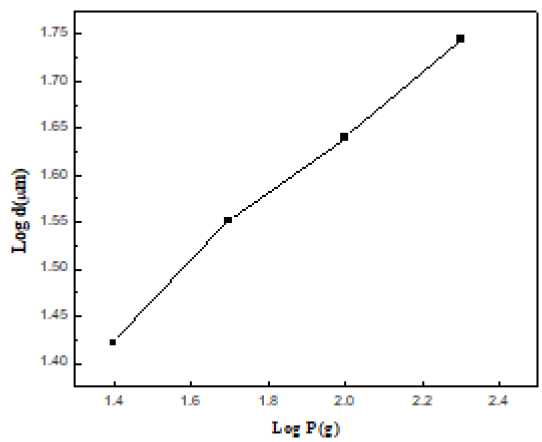

Figure 8: Plot of log P and log d of Succinic acid doped KDP crystal

between 1 and 1.6, then the grown crystal will be a harder material and it is more than 1.6 for soft materials. Since the calculated work hardening coefficient 'n' is more than 1.6, the grown crystal is suggested that it is a soft material and compared to other organic material succinic acid doped KDP nonlinear optical crystal has good mechanical strength. Using the formula $\sigma_y = (H_v/3)(0.1)^{n-2}$, the yield strength of the grown succinic acid doped KDP single crystalline material was calculated. Where σ_y is the yield strength, H_v is the Vicker's hardness and n is the work hardening coefficient. It was calculated as 19.26 MPa from the relation and hence the grown succinic acid doped KDP single crystal has good mechanical strength compared to other kinds of nonlinear optical organic crystals [10].

The ability of a material containing a crack to resist fracture is described as fracture toughness (K_c), which is one of the most important properties of any material for device applications. It was calculated using the formula $K_c = P/\beta C^{3/2}$, where C is the crack length from the center of the indentation, P is the applied load and β (=7) is the geometrical constant for Vickers indenter. The crack length formed in the grown succinic acid doped KDP crystal with the applied load 200g was 88.18µm, from which the fracture toughness was calculated as 20821 kg/m$^{3/2}$. Brittleness is an important property of the crystal which determines its fracture without any appreciable deformation. It is expressed in terms of brittleness index. Using the formula $Bi = H_v/K_c$, brittleness index was calculated as 5796 m$^{-1/2}$. Elastic stiffness constant was calculated from the microhardness by Wooster's empirical relation $C_{11} = (H_v)^{7/4}$[11]. The maximum elastic stiffness constant for the grown succinic acid doped KDP crystal is 43.94x 10^{12}.

Fig. 9 shows the resulting traces of TG/DTA for the succinic acid doped KDP crystal. In the spectrum of thermogravimetric analysis, there is no weight loss of up to 230.55 °C. Hence the crystal is confirmed that it is free from any physically adsorbed water,and it is observed that there is a 5 % weight loss occurring at the temperature 250 °C, which is due to the loss of succinic acid doped components. At 329 °C temperature, nearly 15 % weight of the sample is observed to decompose.The DTA response curve shows three sharp sendothermic

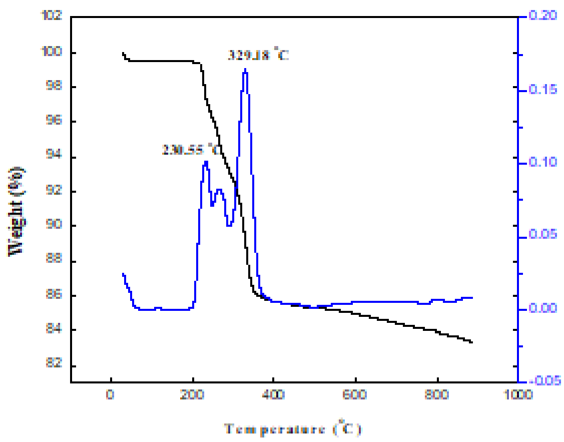

Figure 9: TG/DTA curves of succinic acid doped KDP crystal

peaks at the point where considerable heat is absorbed by the substance to undergo dissociation. Therefore, the grown crystal is stable up to the temperature of 230.55 °C, which is greater than some other doped KDP compound [5], [12-14]. The indexed EDAX spectrum of succinic acid doped KDP single crystal is shown in Fig.10, in which the spectrum reveals the incorporation of dopants 'carbon' in addition to the presence of constituent elements phosphorus, oxygen and potassium of the succinic acid doped potassium dihydrogen phosphate single crystal. Table 2 shows explicitly the weight and atomic percentage of the concentration of dopant in the parent compound.

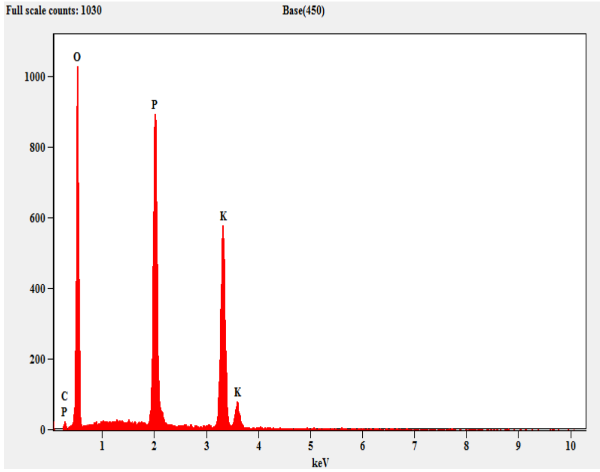

Figure 10: EDAX spectrum of succinic acid doped KDP single crystal

Table 2: Weight and atomic percentage of elements in the succinic acid doped KDP crystal

Element line	Weight%	Weight error	Atom
C K	3.79	± 0.47	6.08
O K	62.51	± 0.74	75.17
P K	16.81	± 0.23	10.44
P L	---	---	---
K K	16.88	± 0.31	8.31
K L	---	---	---
Total	100.00		100.00

5. Conclusions

A nonlinear optical crystal succinic acid doped KDP crystal was grown by a slow solvent evaporation technique. Even though a lot of research is being done on KDP material, since it is a standard one and necessary, compound confirmation was done by X-ray diffraction and FTIR analysis. In the UV-Vis-NIR spectrum, the wide transmittance ranges from ultraviolet to infrared region makes the doped crystal suitable to find application in the deep ultraviolet nonlinear optical device. Since the transmittance in the visible region is sufficiently large enough for SHG device, succinic acid doped KDP single crystal can be used as a good optical material in a laser. From the absorbance spectrum, the optical band gap was measured as 5.6 eV. Second harmonic generation efficiency of succinic acid doped KDP crystal is 1.25 times greater than the standard KDP material. It could withstand a maximum of 200 g load with Vicker's microhardness 120.69 kg/mm^2. By examining various mechanical properties, succinic acid doped KDP crystal has greater strength over than other organic compound doped crystals. The dissociation of the grown crystal starts at 230.55 °C and so it has thermal stability up to the temperature of 230.55 °C, which is greater than the pure and some other doped KDP material. The elements such as carbon and oxygen could be occupied interstitially in the atomic position of potassium dihydrogen phosphate compound and hence mechanical hardness is greater than other doped KDP crystals. The material succinic acid doped KDP is a better candidate over than pure KDP crystal as itposses higher thermal, mechanical stability and SHG efficiency. So, it can be utilized in a laser and photonic device fabrication.

6. Acknowledgement

The authors are very much grateful to the research laboratory SAIF-IIT, Chennai, St. Joseph College, Trichy for extending the facility to study structural, spectroscopic, thermal and mechanical properties of the sample and the Department of Organic Chemistry, IISC, Bangalore, India for second harmonic generation analysis.

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