Effect of Adipic Acid on The Growth And Characterization of Potassium Dihydrogen Phosphate

M. Arthi[1], L.Jothi[2]
[1, 2] Dept of Physics
[1, 2] Namakkal Kavignar Ramalingam Government Arts College for Women, Namakkal - 637001, India.

Abstract- *The Non- Linear optical crystals of adipic acid doped with KDP has been grown by slow evaporation technique at room temperature. The structural parameters of the grown crystals have been determined by powder X- Ray diffraction. The vibrational frequencies of various functional groups in the crystal have been derived from the FTIR spectrum. Optical transparency of the crystal has been determined by UV-Visible studies. Mechanical properties of the grown crystals have been studied using Vickers hardness testes. Further, the fluorescence nature of the sample is analyzed and reported.*

Keywords- Crystal growth, Powder XRD, UV-Visible spectrum, FTIR.

I. INTRODUCTION

Crystal growth technology provides an important basis for many industrial branches. Single crystals with advanced properties play a significant role in the growth of modern scientific world of advanced technology [1, 2]. Organic NLO materials have high figures of merit for a variety of device application. Our research activities on synthesis and crystal growth NLO materials for frequency doubling and also on the synthesis, fabrication and policy of novel covalently functionalized linear and cross linked polymers will received [3]. Recent research is focused on the search for suitable materials displaying excellent second order nonlinear optical properties for potential application in optoelectronics, telecommunication, and optical storage device. A major effect was developed to use non-linear (NLO) optical material to generate different frequencies which are not availed. A single crystal plays a vital role for making precious in some gems, are in industrially used in technological applications, especially in optics and electronics [4]. Single crystals have unique physical properties due to grain with molecules in a strict order and no grain boundaries [5]. They are used for lasers and non- linear optics.

Adipic acid is also known as Hexane- 1, 6 dioxin acid with molecular formula $C_6H_{10}O_4$: Adipic acid is slightly soluble in water and soluble in alcohol and acetone. Adipic acid is used in polyurethane resins, and also in food addictive. Potassium dihydrogen phosphate (KH2PO4) is a transparent dielectric material. A crystallochemical analogue of KDP is widely used in practical applications and is used in microphone, gramophones, and other optical devices. It is often used as a fertilizer, food additive and buffering agent. The salt often co- crystallizes with the dipotassium salt as well as with phosphoric acid. Because of its optical property, the KDP crystals find application in opto-electronics. They are used as commercial non-linear optics materials because of strong transmission stability.

In recent years, adipic acid has been considered as an attractive material for NLO applications, due to their higher non- linear optical properties and also in nucleation and the crystal formation process has cross linking properties. The non- linear property exhibits good transparency level of crystals. Adipic acid has good thermal optical and mechanical properties. Hence, KDP has high brie fringe, high non- linear coefficients frequency, high efficiency of frequency conversion, and high damage threshold against high power laser and it is well known non linear optical material for various optoelectronics applications. Because of its nonlinear optical properties, it has been incorporated into various laser systems for harmonic generation [6]. Owing to this combination of this enhancing physical properties adipic acid doped potassium KDP are used in technological applications and to the applications of non-linear optical materials, it acquires a new significant day by day with the advantage of large number of devices, which is also utilizes laser sources, development of photonics, spectroscopy, fiber optics lines, optical switches, frequency converter and also numerous applications in the medical and pharmacological sectors. Due to these interesting properties we made an attempt to adipic acid doped KDP at particular concentration. In order to prove as grown materials is optically active the title compound has been subjected to various characterizations such as powder XRD, FTIR, UV- Vis, Fluorescence and microhardness studies.

II. CHARACTERIZATION STUDIES

The various characterization techniques have been employed to confirm the grown crystals such as Powder XRD,

FT-IR, UV-VIS-NIR, Fluorescence and Microhardness studies. XRD provides information about crystal structure, phase, crystallinity, and other structural parameters. FTIR identifies chemical bonds in a molecule by producing infra-red absorption spectrum. The function of wavelength is determined by UV-VIS studies. The emitted radiation at longer wavelength is obtained by fluorescence study. Further, the hardness of the grown crystal is estimated by Vickers microhardness method.

III. EXPERIMENTAL

3.1. Crystal growth

Adipic acid doped KDP crystals were grown from aqueous solution of doubly distilled water by slow evaporation method. The equimolar adipic acid and KDP super saturated solution were blended well to attain the homogeneous solution. The solution was stirred with magnetic stirrer for 3 hours at constant room temperature, after attaining the saturated state the solution was filtered and kept without disturbing. The required quantity of adipic acid and potassium dihydrogen phosphate was calculated according to the following reaction,

$$C_6H_{10}O_4 + KH_2PO_4 \rightarrow K\,[C_6H_{12}O_6].PO_2$$

Single crystals with good transparency level are harvested in 10 days. The photograph of grown crystal is shown in Fig.1,

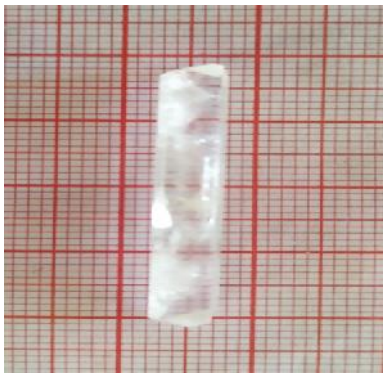

Fig.1.As grown crystal of AKDP

IV. RESULTS AND DISCUSSIONS

4.1. Powder X-ray diffraction analysis

Powder X-Ray diffraction analysis has been carried out to confirm the crystalline nature of the material and provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. Single crystals were obtained for X-ray diffraction analysis of adipic acid (HOOC $(CH_2)_4COOH$) and potassium dihydrogen phosphate (KH_2PO_4) from doubly distilled water solvent system. The grown crystals of AKDP are subjected to X-Ray diffraction analysis. The grown samples were examined with Cu Kα radiation in the range of 1.540 to 1.544 . The resultant Powder X-Ray diffraction pattern of grown crystal AKDP is shown in Fig.2. It consists of prominent peaks corresponding to (100), (110), (200), (210), (211), (310) planes. The highest peak intensity was observed at 247 counts. The calculated values are presented in table.1.The incorporation of dopant in pure crystal lattice was confirmed. Hence the well defined Bragg's peaks at specific 2θ angles show good crystalline materials.

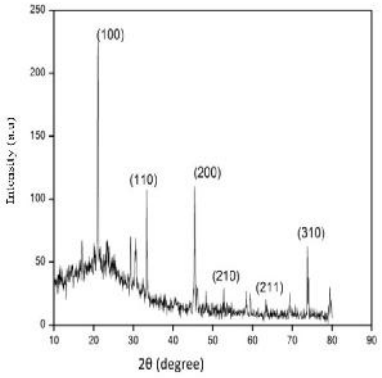

Fig.2.Powder XRD Spectrum of AKDP

Table-1 Powder XRD data of AKDP

2θ	d spacing (Å)	FWHM (mm)
21.14	4.2024	0.1476
30.59	2.9221	0.3936
33.35	2.6859	0.1968
45.41	1.9973	0.1968
73.87	1.2828	0.2952

4.2. Fourier Transform Infrared Spectrum

FTIR are used to define functional group and to investigate the internal and complexion of Polymeric materials and also sensitive changes in molecular structure. It indentifies chemical bonds in the molecule by producing Infrared-

absorption spectrum. The spectra produce a profile of sample for many different compounds. The FTIR spectrum of AKDP was recorded in the range of 4000 cm^{-1} to 400 cm^{-1} using KBr (spectroscopic grade) Pellet Technique which is used as a window material because it is transparent in the IR. It was observed that FTIR spectrum of AKDP in Fig.3 is characterized by many absorption bands, such as, the absorption bands in the range of 2840-3000 cm^{-1} are assigned to C-H bonded molecule. The absorption bands at 721.66, 929.33, and 1708.66 are attributed to C-C stretching vibrations respectively. Most of the absorption bands having different intensities due to this bending and stretching vibrations present of these assignments conform that the presence of various functional groups in the material used for grown crystal and it is tabulated in table.2.

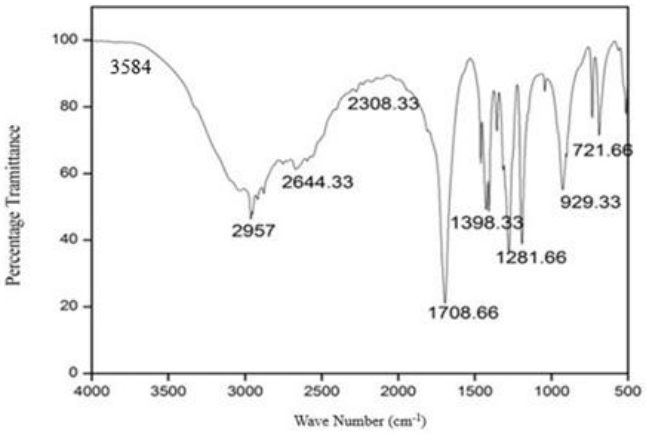

Fig.3. FTIR Spectrum of AKDP

Table-2 Vibrational frequency assignments of AKDP

AKDP Frequency (cm^1)	VIBRATIONAL ASSIGNMENTS
3584	OH stretching
2957	CH_2 asymmetric stretching
2308.33	C=C bonding
1708.66	C=O symmetric stretching
1398.33	CH bending
929.33	Trans = C-H out -of- plane bending
720.66	OH stretching

4.3. UV- Visible Studies

UV-VIS spectroscopy is the quantitative technique used for the determination of chemical substances which absorbs light. The recorded transmission spectrum is shown in fig.4. Transmission spectra are quite important for any doped materials, as it is tool to analyze the interaction between dopant and parent molecule and to know stability for optical application. Hence the optical transmission spectra of the grown crystals were measured in the wavelength range 200nm to 1200 nm using LAMBDA-35 UV-VIS spectrometer. Transmission is the indication of the sample used to analyze transition metal ions, highly conjugated organic compounds and also to determine many other sources. The recorded transmission spectrum of the adipic acid doped KDP crystal is shown in Fig.4, has good transparency in between 200 nm to 1200 nm; it attributes the distribution of molecules in the single crystal.

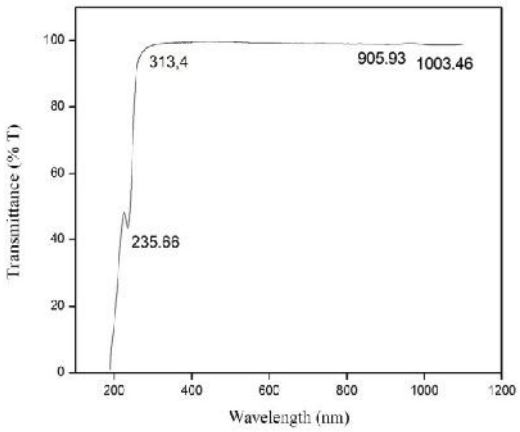

Fig.4. UV Transmission spectrum of AKDP

UV- absorption spectroscopy is used for the determination of impurities in molecules. By measuring the absorbance at specific wavelength, the impurities can be detected. The absorption spectra of adipic acid with KDP shown in Fig.5, the recorded optical spectrum of the adipic acid doped KDP crystal is found to be active in the UV-Visible region having significant absorption in the lower cut-off wavelength of 223.93nm. The lower cut-off wavelength found to be less than 250nm; hence it makes the usefulness of these materials for laser and device applications.

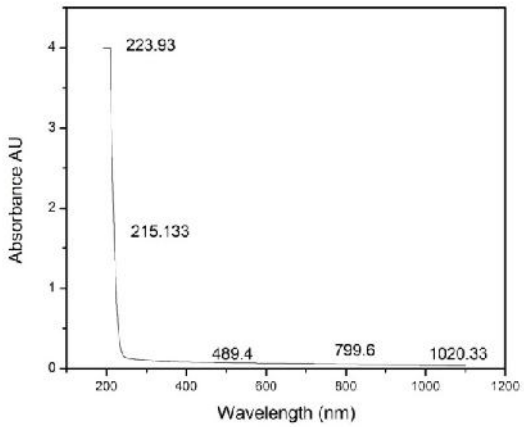

Fig.5. UV Absorption spectrum of AKDP

4.4. Fluorescence Studies

Fluorescence generally found in compounds with low energy π, π^+ transition levels. The ultraviolet and visible regions of the spectrum are of most interest in fluorimetry and absorption in these regions causes the excitation of the outermost electrons of the molecule. Compounds of aliphatic and alicylic carbonyl structures and or highly conjugate double bond structures exhibits florescence [7]. The emission spectrum of AKDP was recorded using JOBINVYON FLUROLOG 3 spectro fluorometer in the range of 200 to 800 nm. The fluorescence of AKDP is shown in Fig.6. The band gap energy of AKDP crystal was found to be 2.69 nm. The higher intensity ratio indicates purity and perfect crystallinity of the title compound.

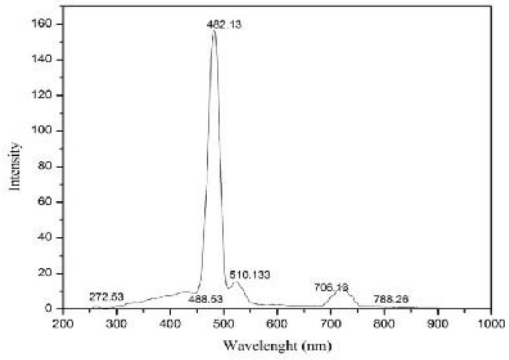

Fig.6. Fluorescence spectrum of AKD

4.5. Microhardness studies

Hardness of a material is a measure of its resistance, it offers to local deformation.The microhardness of the grown crystals was measured by using Vicker's hardness test. Single crystals are performed to evaluate the mechanical propertites and to examine the resistance against applied load. Microhardness studies provide useful information regarding stability, elastic constant, strength of the materials used. Since the test indentation is very small in a Vickers test, it is useful for a variety of applications: testing very thin materials like foils or measuring the surface of a part, small parts or small areas, measuring individual microstructures, or measuring the depth of case hardening by sectioning a part and making a series of indentations to describe a profile of the change in hardness [8]. The plot between load (p) and hardness number (HV) is shown in Fig.7.

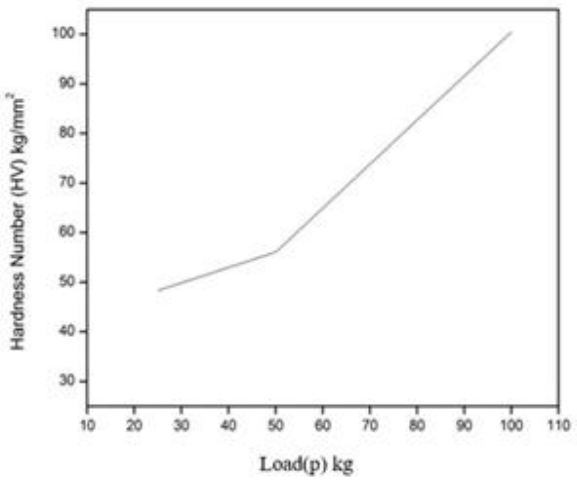

Fig.7. Vicker's hardness for AKDP crystals

The plot between log p against log d for AKDP crystal is shown in Fig.8. The slope of the straight lines of the Fig 8 gives the work hardening coefficient (n). The microhardness number increases with increase in load. The obtained value for AKDP crystal is 2.0, which is used in the category of soft materials and also in non-linear optical applications[10].

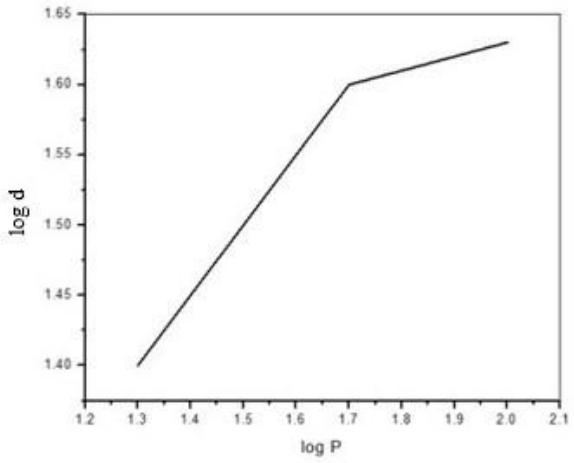

Fig.8. Graph between log p and log d

V. CONCLUSION

A new crystal of adipic acid with potassium dihydrogen phosphate (AKDP) has been grown by slow evaporation using doubly distilled water. The sharp well defined peak in powder XRD spectrum confirms the crystalline nature of the material. AKDP crystal is optically transparent in the entire visible region with 90% transparency level. The various functional groups of the compounds are analyzed by using FTIR techniques. The obtained transmission and absorption curves give the transparency and impurity level of the grown crystalline material. The presence of carbonyl groups is determined by Fluorescence study. Work hardening coefficient of the AKDP crystal was determined from microhardness study and their mechanical stability was conformed.

VI. ACKNOWLEDGEMENT

The authors are thankful to Mr. Y. Vincent Sayagaraj, Archbishop Instrumentation centre, St. Joseph's College, Tiruchirappalli for Powder X-ray diffraction, FTIR, UV, Flurescence and microhardness characterization studies.

REFERENCES

[1] G.M. Arunmozhi, E. Gomes, S. Ganesamoorthy, Cryst. Res.Technol. vol.39, no.5, 408-413, 2004.
[2] R. Rajasekaran, P.M. Ushashree, R. Jayavel, P. Ramasamy, J. Cryst. Growth, 229, 563-567, 2001.
[3] A. S. Haja Hameed, C. W. Lan, J. Cryst. Growth, vol.5, no.2, 475 - 480, 2004.
[4] P. SanthanaRaghavan, P. Ramasamy, Crystal Growth processes and methods, K.R.U.Publication, Kumbakonam, 2000.
[5] G. Bhagavannarayana, S. Parthiban, S.Meenakshisundaram, Cyst. Growth and Design, vol.2, no.8, 446-451, 2008.
[6] J.S. Liu, J.J. Liu, Y.Tang, Laser Phys. 18, vol.3, no.7, 1124, 2008.
[7] L. Jothi, R.Babu, K. Ramamurthi, Journal of Minerals and Material Characterization and Engineering, vol.2, no.4, 308-318, 2014.
[8] B.W. Mott, Micro Indentation Hardness Testing, vol.2, no. 9, 308-313, Butterworth, London, 1966.
[9] S.A. Martin Britto Dhas, S. Natarajan, Cryst. Res.Technol., vol. 42, no. 5,471-476, 2007.
[10] E.M. Onistsch, Microskope 95, vol.2, no.10, 1950.