Scientific Journal of Impact Factor (SJIF): 5.71
e-ISSN (O): 2348-4470
p-ISSN (P): 2348-6406

International Journal of Advance Engineering and Research Development

International Conference on Momentous Role of Nanomaterials in Renewable Energy Devices

Volume 5, Special Issue 07, April-2018 (UGC Approved)

Spectral, Thermal, Electrical and Mechanical Properties of Potassium Fumarate Dihydrate (PFD) Single Crystals

A.T. Ravichandran[1*], K. Mangaiyarkarasi[1], A. Manivel[2]

[1]PG & Research Department of Physics, National College (Autonomous),
Tiruchirappalli-620 001, Tamil Nadu, India
[2] PG & Research Department of Chemistry, Saraswathi Narayanan College (Autonomous),
Madurai-625 022. Tamil Nadu, India

Abstract — *Potassium Fumarate Dihydrate (PFD) single crystal was successfully grown by conventional slow evaporation technique at room temperature. Fourier transform infrared spectroscopic analysis was performed for the identification of functional groups present in the crystal. UV–vis–NIR transmittance spectrum was recorded in the region of 200–1100 nm, which evidenced the good optical transparencies of the obtained crystals. The transmittance curve showed the lower cut-off wavelength at 308 nm. Dielectric constant and dielectric loss were measured for the grown PFD crystals in the frequency range from 50 Hz to 12 kHz at four different temperatures namely 303, 323, 343 and 363 K. The dielectric constant was observed to be little higher at low frequency region and decreases with increasing frequency. The thermal stability of the grown crystal was investigated by using TG-DTA analysis. The grown crystal was thermally stable up to 850° C. In TG-DTA spectrum, three stages of decomposition have been observed. The AC conductivity study using complex impedance spectroscopy was performed to characterize the bulk resistance of the grown crystal. Vickers micro-hardness study was carried out to understand the mechanical properties of the grown crystal with varying loads ranging from 5 to 200 g. The hardness of the titled compound increases on increasing the load and obeyed the reverse indentation size effect. The Meyer's index number (n) has been calculated for the grown potassium fumarate dihydrate (PFD) crystal as 2.14 suggest the PFD crystal belongs to soft material category. It was observed from results that the yield strength and stiffness constant are increasing with increase in the applied load. This finds the suitability of the single crystal for various thermo mechanical applications.*

Keywords- *Potassium fumarate dihydrate; single crystal growth; spectral studies; dielectric analysis; electrical study; micro hardness.*

I. INTRODUCTION

Organic materials have high optical property, optical susceptibility, optical threshold and low frequency dispersion and have low melting point, low mechanical strength, high degree of delocalization due to their weak Van der Waal's and hydrogen bonding and also they have the flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high laser damage threshold values [1-3]. Inorganic NLO materials possess high melting point, high mechanical strength, and high degree of chemical inertness but poor optical nonlinearity. To consider the advantages of both organic and inorganic NLO materials, many researchers concentrate on metal organic complexes such as L-arginine phosphate, L-histidine tetrafluoroborate, L-cystine hydrochloride, L-arginine hydrochloride and the lithium compounds lithium iodate, lithium niobate and lithium tantalate etc [4-10]. Fumaric acid is receiving much attention because of their interesting physic-chemical properties. Alkali metals, in spite of having important metallic properties such as high electric and thermal conductivity, have received less attention to the growth and characterization of these elements as metallic fumarate [11]. Alkali metals are more metallic in character than alkaline earth and transition metals because the valence shell electron of the former is loosely bound to their atoms. However, information about single crystal growth of potassium fumarate is available, its characterization and properties in the form of single crystals is not available in the literature [12-14]. Hence it is worthwhile to grow potassium fumarate in the form of single crystals and study their properties which may lead to detailed knowledge about their utilization in different electronic devices. Growth and characterization of metal fumarate crystals like lithium fumarate, L-alaninium fumarate, L-valinium fumarate and terbium fumarate etc have been carried out and reported in the literature [11,14-16]. The crystal structure of potassium fumarate dehydrate crystal was solved by Gupta et al [12]. The present study deals with the growth of potassium fumarate by slow evaporation technique and its characterization. The present investigation is focused on the growth and characterization of crystals of potassium fumarate dihydrate (PFD), a new semi organic material. The PFD crystals are grown by slow evaporation technique at room temperature. In this work, bulk growth, spectral, structural, thermal, electrical and mechanical properties of potassium fumarate dihydrate (PFD) crystals were carried out for the first time and the results are presented and discussed.

II. EXPERIMENTAL

A. Synthesis and growth of PFD crystals

Potassium fumarate was synthesized by using analytical grade potassium hydroxide and fumaric acid in the molar ratio of 2:1 in Millipore water. Potassium hydroxide was dissolved in the Millipore water and the fumaric acid was added to react with the potassium hydroxide. Fully dissolved solution was stirred well and evaporated to obtain PFD salt. Re-crystallization was carried out to improve the purity of the synthesized PF salt. Solution method with slow evaporation technique was adopted to grow crystals of the synthesized PF salt. The saturated solution of PFD sample was prepared and constantly stirred for about 6 hours using a magnetic stirrer and was filtered using 4 micron Whatmann filter paper. Then the filtered solution was taken in a beaker and covered by perforated cover for controlled evaporation.

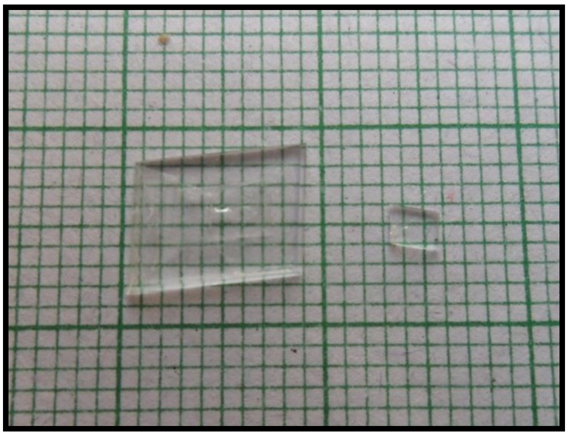

Figure 1. Obtained seed and grown crystal of potassium fumarate dihydrate

The seed crystals of PFD were obtained by spontaneous nucleation. The supersaturated solution of PFD was carefully transferred into another glass beaker and kept at room temperature. Two or three good quality seed crystals of PFD were placed in the supersaturated solution and the solution was allowed to evaporate the solvent slowly into atmosphere. A typical single crystal with size10 mm x 8 mm x 3 mm was obtained within a period of 45 days. A grown crystal is shown in figure 1 and the grown crystals are found to be stable, non-hygroscopic at ambient temperature and well transparent.

III. RESULTS AND DISCUSSION

A. Single crystal X-ray diffraction study

Single crystal X-ray diffraction studies for a potassium fumarate dihydrate single crystal were carried out using a Bruker AXS Kappa apex II CCD diffractometer. The wavelength of incident MoKα radiation is 0.7107 Å. Single crystal XRD pattern is shown in Fig.2. The regular arrangement of spots on the pattern indicates the single crystallinity of the grown crystal. The obtained single crystal XRD data are given in the table 1. The grown potassium fumarate dihydrate (PFD) crystal crystallizes in monoclinic system and this result is coincident with the data reported in the literature [12].

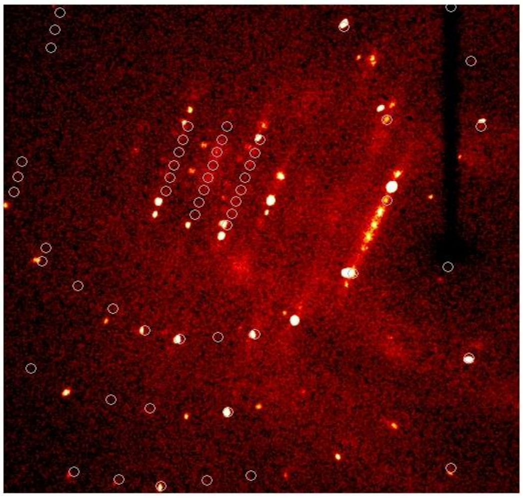

Figure 2. Single crystal XRD pattern for potassium fumarate dehydrate

Table 1. Crystallographic data for potassium fumarate dihydrate crystal

Diffractometer	Bruker AXS Kappa II CCD diffractometer.
Radiation, wavelength	MoK_{α}, 0.71069 Å
Refinement method	Full matrix Least square method
Chemical formula	$K_2C_4H_2O_4 . 2 H_2O$
Crystal color	Colorless, transparent
Temperature	293(2) K
Symmetry	Monoclinic
Space group	$P2_1/c$
a	6.366 (3) Å
b	18.274 (3) Å
c	7.275(2) Å
α	90°
β	98.32°
γ	90°
Volume	837.42 (3) $Å^3$
Z	4

B. Fourier Transform Infrared (FTIR) spectroscopic studies

FTIR absorption spectrum of the grown PFD crystalline sample was recorded using SHIMADZU (FTIR-8400S) in the range of 400-4000 cm^{-1} and it is shown in the figure 3. The functional groups of the grown crystals were confirmed by Fourier Transform Infrared spectrum. The broad and strong absorption band around 3415 cm^{-1} and 3296 cm^{-1} may be due to the presence of water and OH stretching mode of vibration. The two peaks associated with the asymmetric (ν_{as}) stretching vibrations and symmetric (ν_s) stretching vibrations of deprotonated carboxylate groups (-COO-) were appeared at 1570 cm^{-1} and 1380 cm^{-1}, respectively. The difference between the asymmetric stretching vibrations and symmetric stretching vibrations ($\Delta\nu$) is about 190 cm^{-1}, shows that the bridging mode of carboxylate groups. It is known from the literature that $\Delta\nu$ below 200 cm^{-1} may be observed for the bidentate carboxylate species and the $\Delta\nu$ values above 200 cm^{-1} could be seen for the monodentate carboxylate moieties. The observed $\Delta\nu$ = 190 cm^{-1} shows the bidentate nature of the formed PFD crystals. The peaks resulting from -C=O stretching were observed at 1695 cm^{-1} and 1642 cm^{-1}. The strong band at 1222 cm^{-1} may be attributed to the in-plane deformation and band at 1011 cm^{-1} may be due to the symmetric C-C stretching vibrations. The sharp peaks observed at 821 cm^{-1} may be due to the in-plane bending motion of-O-C-O. A peak at 579 cm-1 may be due the C-C=O wagging. A peak at 537 cm-1 may be attributed to the presence of metal oxygen bond. The peaks around 722 and 664 cm-1 is due to the COO^- bending vibrations. The spectral assignments are given in accordance with the data reported in the literature [15]. The complete spectral assignments for potassium fumarate dihydrate (KFD) crystal are provided in the table 2.

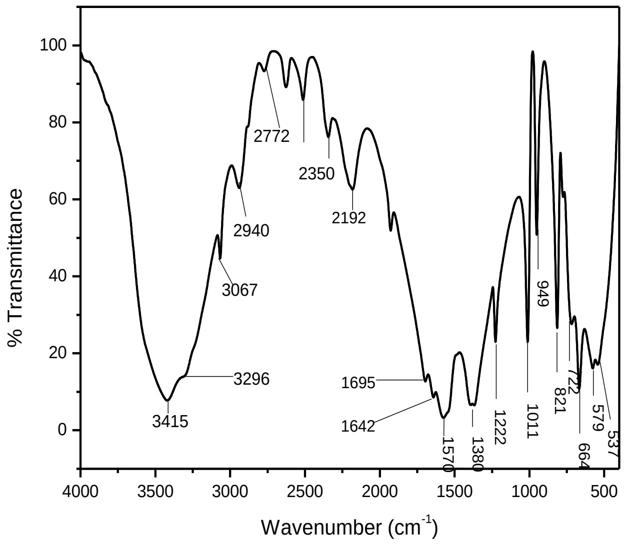

Figure 3. FT-IR spectra of potassium fumarate dihydrate crystal

Table 2. FTIR spectral assignments for potassium fumarate dihydrate sample

Wavenumber (cm^{-1})	**Assignment**
3415	H_2O
3296	OH stret.
3067	CH stretc
2940	asym -CH stretc
2772	sym-CH stretc
2350	CO_2
2192	C=C asym stretch
1695	-C=O stretc
1642	-C=O stretc
1570	$-COO^-$ asym. stretc
1380	$-COO^-$ sym. stretc
1222	-CO- stretc
1011	-C-C- bending
949	-C-C- stretching
821	-O-C-O in plane bending
722	COO^- bending
664	COO^- bending
579	C-C=O wagging
537	Metal oxygen bond

C. Optical transmittance studies

Optical transmittance range, transparency cut-off and the absorbance band are important parameters to tailor the NLO materials for specific applications. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons [17]. The crystal is well polished and the specimen of 1.5 mm thickness was subjected to transmission measurements using Lambda 35 UV-Vis-NIR spectrophotometer in the spectral region of 200-1100 nm. There is no appreciable absorption of light in the entire visible range. For optical fabrications, the crystal should be highly transparent in a considerable region of wavelength [18,19]. Figure 4 shows the transmission curve, in which the lower cut-off wavelength is obtained at 308 nm and the transparency in the entire visible region for this crystal suggests its suitability for second harmonic generation. Using the formula, $E_g = hc/\lambda$, the band gap energy was found to be 3.24 eV. According to Tauc relation, the absorption coefficient α of a material is given by [20,21].

$$\alpha h\nu = A(h\nu - E_g)^n$$

where E_g is the energy gap, A is a constant and is different for different transitions, $h\nu$ is the energy of photon and n is an index which assumes the values ½ , 3/2 and 2 depending on the nature of electronic transitions responsible for absorption. The E_g value could be estimated from the plot $(\alpha h\nu)^{1/2}$ versus photon energy (inset of figure). The plot $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ was drawn and optical band gap (E_g) value was obtained from the interception of the linear portion of the curve with X-axis. This gives the E_g value of direct band gap character around 3.24 eV for potassium fumarate crystal.

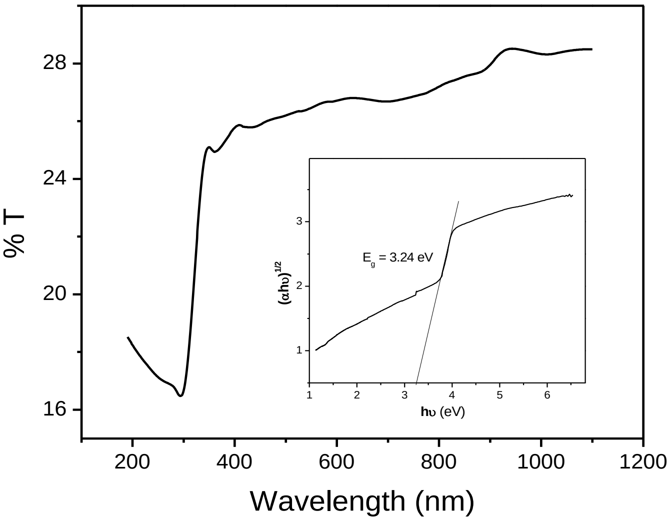

Figure 4. UV-visible transmittance spectrum of potassium fumarate dihydrate crystal. Inset shows the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (Tauc plot)

D. TG/DTA studies

The thermal stability of the grown crystal was investigated by using TG-DTA analysis. The typical TG/DTA curve is shown in figure 5. The grown crystal is thermally stable up to 850° C. In TG-DTA spectrum, three stages of decomposition have been observed and in the first stage weight loss around 100 °C evident the presence of water molecules in the grown crystal. The weight loss around 400 °C and 800 °C may be attributed to the decomposition of organic and inorganic part respectively.

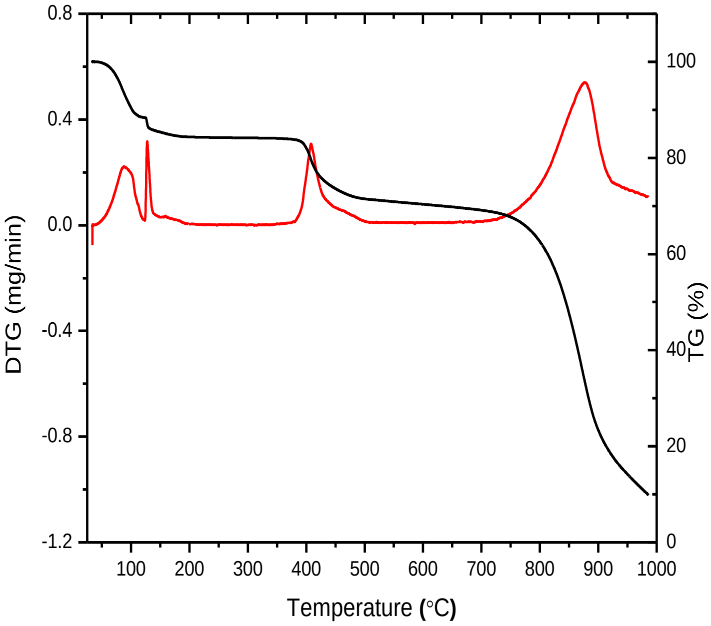

Figure 5. TG/DTA curve of potassium fumarate dihydrate crystal.

E. Dielectric Studies

The well polished and good quality single crystal was subjected to dielectric measurements by using Agilent LCR meter equipped with resistive furnace and which is connected with a temperature controller having the accuracy of ±2 ◦C. A thin coating of carbons was applied on both the surfaces of the samples for firm contact. Then the crystal was placed between the two copper electrodes to form the parallel plate capacitor.

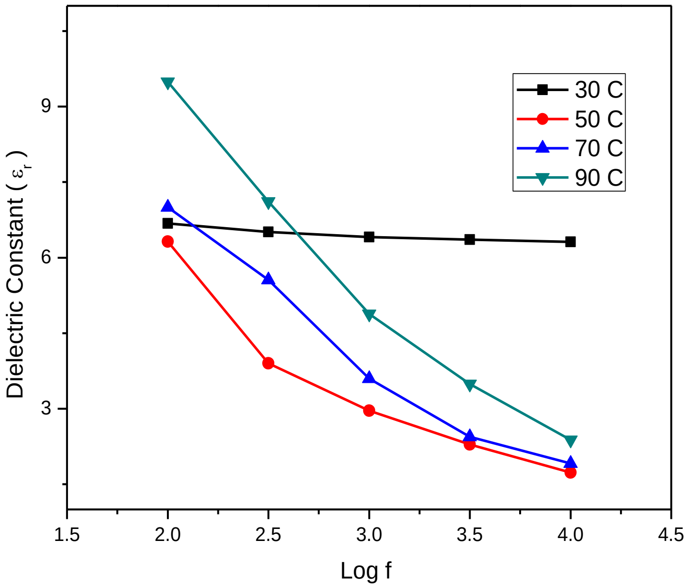

Figure 6. Variation of dielectric constant with frequency at different temperatures

The capacitance and dissipation factor of the specimen were measured as a function of frequency. From that dielectric constant (ε) and dielectric loss (ε″) of the material was calculated using the following relation.

$$\text{Dielectric constant } (\varepsilon) = c.d / \varepsilon_0.A$$

$$\text{Dielectric loss } \varepsilon'' = \varepsilon \tan \delta$$

where, C is the capacitance, A is the area of the plate, d is the distance between the two parallel plates. ε_0 is the absolute permittivity of the free space ($\varepsilon_0 \approx 8.854 \times 10^{-12}$ F / m). Figure 6 shows the variation of dielectric constant as a function of applied frequency range from 50 Hz to 12 kHz at four different temperatures namely 303, 323, 343 and 363 K. It could be observed from the figure 6 that in high frequency region, dielectric constant is almost constant but in lower frequency region, and decreases with increasing frequency. The magnitude of dielectric constant depends on the degree of polarization of charge in the crystal and that is arises from the contribution of different polarizations, namely electronic, ionic, orientation and space charge polarization. The high value of dielectric constant at low frequency is due to the presence of space charge polarization. Space charge polarization arises due to the mobile charge carriers impeded by interfaces. The space charge polarization depends on the bonding, structure, purity and perfection of the crystal.

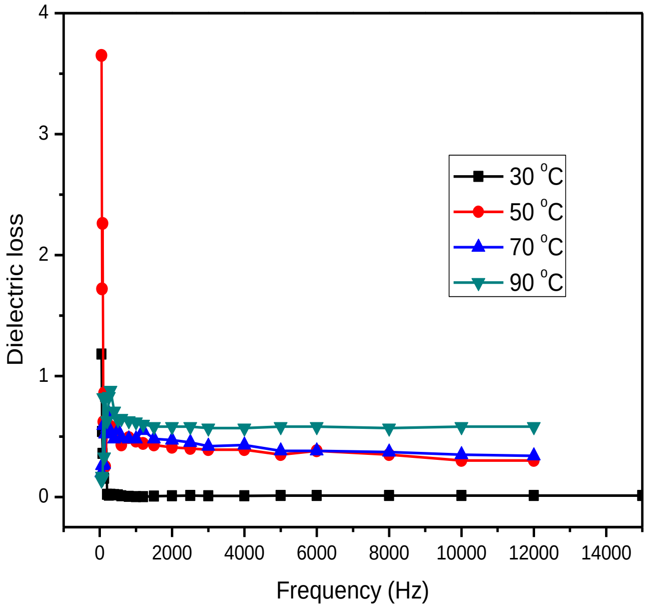

Figure 7. The variation of dielectric loss as a function of frequency at different temperatures

The variation of dielectric loss as a function of frequency at room temperature is shown in Figure 7. These curves suggest that dielectric loss is also strongly dependent on the frequency of the applied field. The higher values of dielectric loss at low frequencies originate from space charge polarization mechanism dipoles. The characteristic of low dielectric loss at high frequencies classifies that the enhanced optical quality nature of the grown sample with lesser defects. And also the experimental dielectric loss decreases with increase in frequency at almost all temperatures but appears to achieve saturation in the higher frequency range of 12 kHz and above, at all the temperatures ranging from 303 K to 363 K. The characteristic of low dielectric loss with high frequency suggests that the sample possess good optical quality with lesser defects and which is an important criterion for considering the materials for photonics, electro – optic and NLO applications [22,23].

F. High temperature AC impedance analysis

The AC conductivity study using complex impedance spectroscopy is performed to characterize the bulk resistance of the grown crystal. The measurement of complex impedance response to small AC signals was carried out in the frequency range of 100 Hz to 15MHz at different temperatures. The typical impedance curves obtained for the PFD crystals at different temperatures were presented in figure 8. Incomplete semicircles were obtained at low temperatures and this may be owing to the very large resistivity of the crystal at low temperatures. The diameter of the semicircle arch and bulk resistance get decreased with increasing temperature.

The AC conductivity of the grown crystals can be determined from the real part of the impedance. The electrical conductivity is proportional to temperature. The AC conductivity shows a linear Arrhenius behavior indicating that the charge carriers are band conduction electrons.

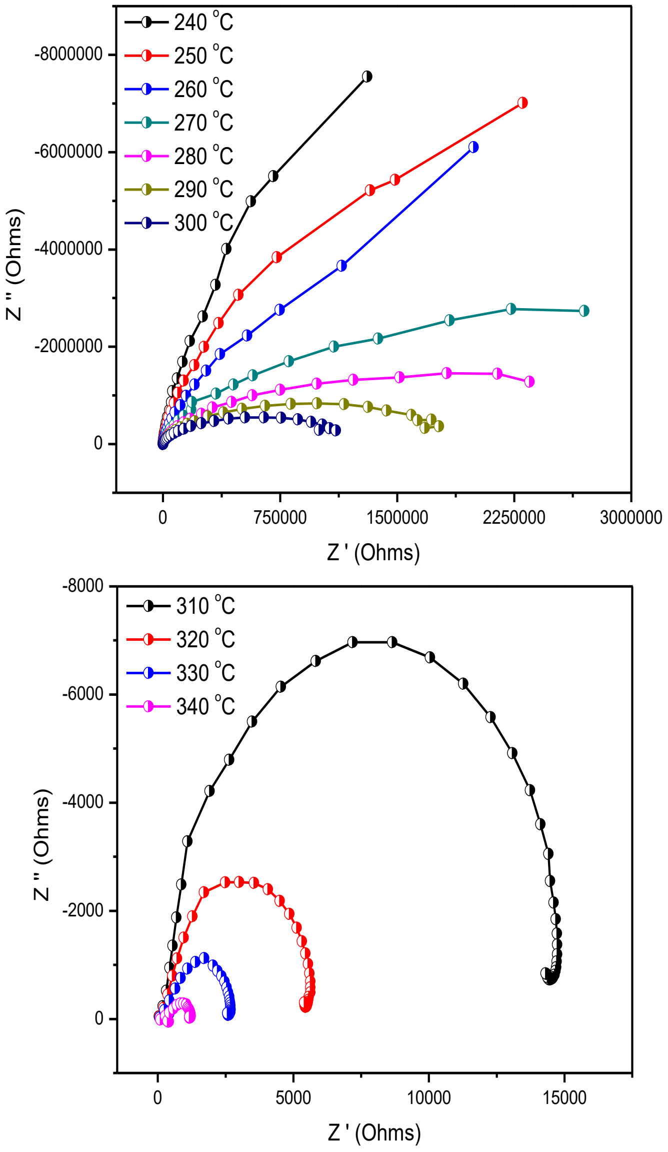

Figure 8. AC-impedance analysis of PFD recorded at different temperatures.

G. Mechanical studies

The resistance offered by a crystal to the motion of dislocation, deformation or damage under an applied stress is measured by the hardness of the crystal. During the making of NLO crystals mechanical stress is applied on the crystal while cutting and polishing. So it is necessary to know the mechanical stress the crystals can withstand without any crack. The ratio of the applied load to the projected area indentation gives the hardness.

The mechanical strength of the grown crystal was determined by micro-hardness test. The micro-hardness test was carried out using Leitz-Weitzler Vickers micro-hardness tester which was fitted by diamond pyramidal indenter. The hardness value was calculated using the following equation.

$$H_v = 1.8544\ P / d^2\ \ (\text{kg/mm}^2)$$

Where, H_v is the hardness value, P is the applied load in gram and d is the diagonal indentation length in mm and 1.8544 is a constant of a geometrical factor for the diamond pyramidal indenter [24]. The variation of the obtained hardness number with the applied load for potassium fumarate crystal is shown in the Figure 9.

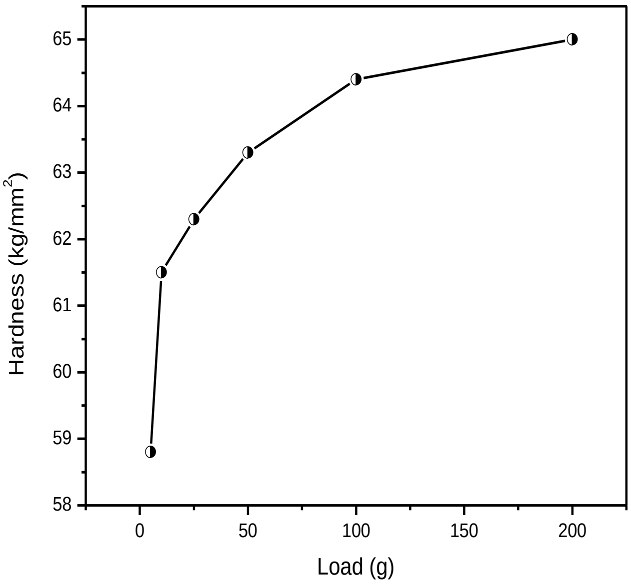

Figure 9. Dependence of Vickers micro hardness on load of PFD crystal

From the results, it is observed that hardness number increases with load obeying the reverse indentation size effect. According to Meyer's law, $P=ad^n$, where 'n' is the Meyer's index and 's' is an arbitrary constant for a given material. The plot of log P versus log d is a straight line and the slope of the line gives 'n' (Figure 10). From careful observations on various materials, Onitsch [25] pointed out that n' lies between 1 and 1.6 for moderately hard materials, and it is more for soft materials. The value of 'n' obtained for grown potassium fumarate dihydrate (PFD) crystal was 2.14. Thus PFD crystal belongs to soft material category.

Yield strength is the maximum stress that can be developed in a material without causing plastic deformation and it is the stress at which a material exhibits a specified permanent deformation. Stiffness is the rigidity of an object and its complementary concept is flexibility. Stiffness is a measure of the resistance offered by an elastic body to deformation or pliability.

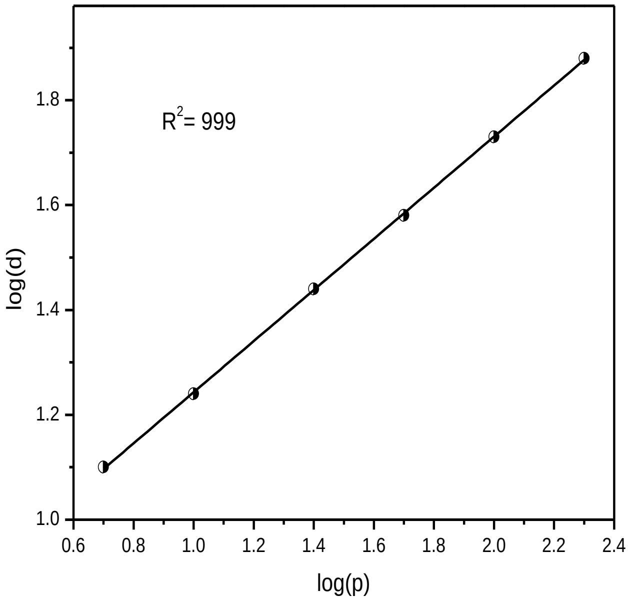

Figure 10. Plot of log P versus log d

Using the micro-hardness data, the yield strength and stiffness constant have been determined. Yield strength of the material can be found out using the relation, yield strength (σ_y) = (H_v / 3) and the stiffness constant (C_{11}) for different loads was calculated the formula $C_{11} = H_v^{7/4}$ where H_v is the micro-hardness of the material [26].

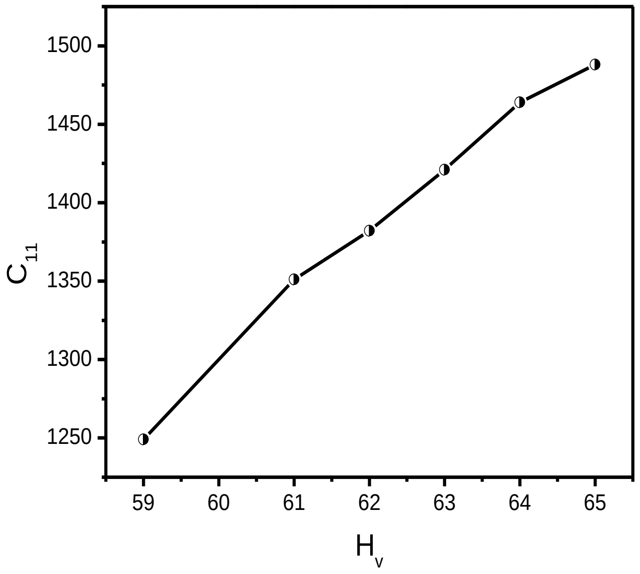

Figure 11. Variation of stiffness constant with respect to different applied loads

The variations of yield strength and stiffness constant with the applied load for potassium fumarate dihydrate crystal are presented in the figures 11 and figure 12 respectively.

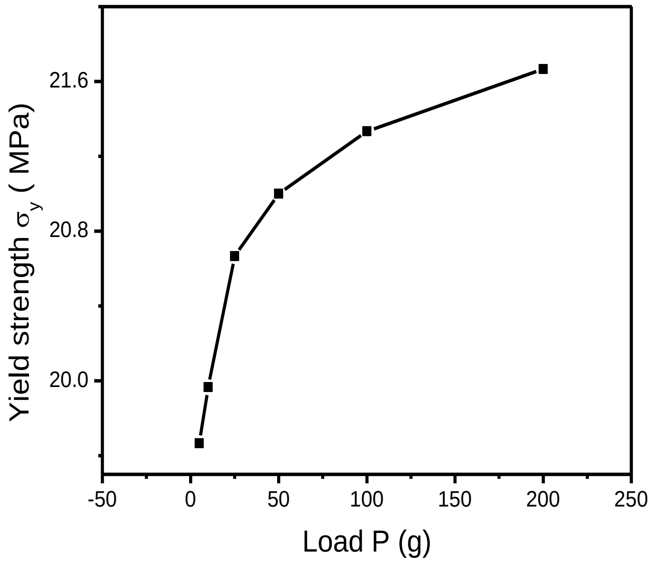

Figure 12. Variation of yield strength with respect to different applied loads

From the results, it is observed that the yield strength and stiffness constant are increasing with increase in the applied load. As the values of yield strength and stiffness constant are high, the resistance of plastic to bending and tightness of bonding between neighboring atoms will be high and the potassium dehydrate crystal has the strong binding between the ions.

IV. CONCLUSION

The single crystals of pure Potassium fumarate dihydrate were grown by slow evaporation technique. Optical transparency of the grown crystal was checked by optical studies and the optical band gap of potassium fumarate crystal was found to be 3.24 eV. The functional groups of the grown crystal have been identified by FTIR method. The dielectric studies were carried out for different frequencies and with different temperatures. It is found that the dielectric constant and dielectric loss of PFD decreases with increase of frequency and confirms that the crystals possess good optical quality with lesser defects which is of vital importance for non-linear optical materials. Mechanical properties of the PFD were explored by using Vickers micro-hardness study. The hardness of the titled compound increases on increasing the load and obeys the reverse indentation size effect. The observed Meyer's index value suggests that PFD crystal belongs to soft material category. From the results, yield strength and stiffness constant were calculated and the obtained results were discussed.

REFERENCES

[1] S.B Monaco, L.E. Davis, S.P. Velsko, F.T. Wang, D. Eimerl and A Zalkin, "Synthesis and characterization of chemical analogs of L-arginine phosphate", *J. Crystal Growth*, vol. 85, pp. 252-255, November 1987.

[2] K.J. Arun and S. Jayalakshmi, "Growth and Characterization of Nonlinear Optical Single Crystals of L-Alaninium Oxalate", *J. Min. Mater. Charact. Eng*. Vol. 8, pp.635-646, August 2009.

[3] G. Madurambal, M. Mariyappan and S. Monojumdar , "Thermal, UV and FTIR spectral studies of urea–thiourea zinc chloride single crystal" *J. Therm. Anal. Calorim*. vol. 100, pp.763-768, January 2010.

[4] R. Ittyachan and P. Sagayaraj, "Growth and characterization of a new promising NLO L-histidine bromide crystal", *J. Crystal Growth*, vol. 249, pp. 557-560, March 2003.

[5] U. Chatterjee, A.M. Rudra and G.C. Bhar "Generation of 6.8–7.7 µm radiation in lithium iodate" *Appl. Phys. B*, vol. 61, pp.489-491.(November 1995.

[6] F. Laeri, R. Jungen, G. Angelow, U. Vietze, T. Engel, M. Wuïrtz and D.Hilgenberg, "Photorefraction in the ultraviolet: Materials and effects" *Appl. Phys. B*, vol. 61, pp. 351-360, October 1995.

[7] L. N. Rashkovich and B.Y. Shekunov, "Study of the growth mechanism of L-arginine chloride monohydrate (LACh) crystals", *J. Crystal Growth*, vol.112, pp. 183- 191, May 1991.

[8] M.D. Aggarwal, J. Choi , W.S.Wang, K. Bhat, R.B. Lal and A.D. Shields, "Solution growth of a novel nonlinear optical material: L-histidine tetrafluoroborate", *J. Crystal Growth*, vol. 204, pp. 179-182. July 1999

[9] D.Rajan Babu, D.Jayaraman, R.Mohankumar and R.Jayavel, "Growth and characterization of non-linear optical L-alanine tetrafluoroborate (L-AlFB) single crystals" *J. Crystal Growth*, vol. 24, pp.121-125, November 2002.

[10] V. Gopalan and M.C. Gupta, "Observation of internal field in $LiTaO_3$ single crystals: Its origin and time-temperature dependence" *Appl. Phys. Lett*. vol. 68, pp. 888-890, Febraury 1996.

[11] B. Want and M.D.Shah, Growth and characterization of terbium fumarate heptahydrate single crystals, *Journal of Crystal Growth*, vol. 389, pp. 39–46, March 2014.

[12] M.P. Gupta and W.H Barnes, The Potassium salt of Fumaric acid: Preparation Unit cell constants, space groups, and X-ray diffraction Powder identification data" *Canadian Journal of Chemistry*, vol. 39, 1961, pp. 1739-1745, September 1961.

[13] E.Y. Ionashiro, F.J. Caires, A.B. Siqueira, L.S. Lima and C.T. Carvalho, Thermal behaviour of fumaric acid, sodium fumarate and its compounds with light trivalent lanthanides in air atmosphere, *J. Therm. Anal. Calorim*. vol. 108, pp. 1183–1188, May 2011

[14] A. Arunkumar and P. Ramasamy, "Synthesis, crystal growth and structural characterization of lithium fumarate semi-organic single crystals", *Materials Letters*, vol. 123, pp. 246–249, May 2014.

[15] C. Ramachandra Raja and A. Antony Joseph, "Crystal growth and characterization of new nonlinear optical single crystals of l-alaninium fumarate" *Materials Letters*, vol. 63, pp. 2507–2509, November 2009.

[16] C. Ramachandra Raja and A. Antony Joseph, "Synthesis, spectral and thermal studies of new nonlinear optical crystal: l-valinium fumarate" *Materials Letters*, vol. 64, pp.108–110, January 2010.

[17] N. Tigau, V. Ciupina, G. Prodan, G. I.Rusu, C. Gheorghies and E. Vasile, "Influence of thermal annealing in air on the structural and optical properties of amorphous antimony trisulfide thin films" *J. Optoelectronics and Adv. Mater*. Vol. 6, pp. 211-217, March 2004.

[18] V. Krishnakumar and R. Nagalakshmi, "Crystal growth and vibrational spectroscopic studies of the semiorganic non-linear optical crystal—bisthiourea zinc chloride", *Spectrochim. Acta A*, vol. 61, pp.499-507, January 2005.

[19] V. Krishnakumar and R. John Xavier, "FT Raman and FT–IR spectral studies of 3-mercapto-1,2,4-triazole" *Spectrochim. Acta A*, vol. 60, pp. 709-714, February 2004.

[20] J. Tauc, "Amorphous and Liquid Semiconductors" Plenum, New York, 3rd ed, 1974.

[21] S. Sirohi and T.P. Sharma, "Band gaps of cadmium telluride sintered film" *Optical Materials*, vol. 13, pp. 267-269, November 1999.

[22] S. Suresh, "Growth, optical, mechanical and electrical studies of nonlinear optical crystal: L-Valinium oxalate", *Optik*, vol. 125, pp. 5842–5845, October 2014.

[23] A.S.J. Lucia Rose, P. Selvarajan and S. Perumal, "Growth, structural, spectral, mechanical and dielectric characterization of RbCl-doped L-alanine hydrogen chloride", *Physica B: Physics of Condensed Matter*, vol. 406, pp. 412-417, February 2011,

[24] A. Shanthi, C. Krishnan and P. Selvarajan, "Growth and characterization of a single crystal of Urea Adipic acid (UAA)–A third order nonlinear optical material" *Spectrochimica Acta Part A* Vol. 122, pp. 521–528, March 2014.

[25] E.M. Onitsch, "Micro-hardness Testing", *Mikroskopie* vol. 95, pp. 12-14. January 1950

[26] V.Kathiravan, P.Shanmugam, S.Pari and P.Selvarajan, "Structural, dielectric and hardness parameters of L-arginine hydrochloride crystals doped with L-tartaric acid", *Int. J. Adv. Sci. Technical. Res*. vol. 4, pp. 420-429. April. 2014.