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Synthesis, Optical, Thermal and Dielectric Studies on Novel Semi Organic Non Linear Optical Crystal by Solution Growth Technique

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Abstract: Single crystals of Urea Potassium Chloride (UPC) have been grown from aqueous solution by slow evaporation technique. The grown crystal was carried out by X-ray diffraction (XRD) methods and it is observed that the samples crystallize in hexagonal system with non-centrosymmetric space groups. The modes of vibrations of different molecular groups present have been identified by spectral analysis. The optical analysis shows the existence of wide transparency window suitable for optoelectronic applications with bandgap energy of about 5.64 eV. The thermal behaviour of the grown crystal was investigated by thermo gravimetric and differential thermal analysis. Photoconductivity studies revealed the positive photo conducting nature. The dielectric measurements were carried out to determine the dielectric behaviour of the crystal. The SHG efficiency of UPC crystal was found to be 1.3 times that of potassium dihydrogen phosphate (KDP) crystal. The growth mechanism and surface features are investigated by using scanning electron microscope (SEM). The hardness of the sample was tested by microhardness test which shows that the grown crystal belongs to the soft category of materials.
Keywords: Growth from solution, Nonlinear optical crystal, Dielectric studies, Optical properties.

1. Introduction

Non-linear optical (NLO) materials have played a vital role in Laser science and optical information storage devices. UPC is a desirable semi-organic non-linear optical which exhibits low angular sensitivity and hence useful for second harmonic generation SHG [1-5]. In these materials, high optical non-linearity of pure organic compound is combined with the favourable mechanical and thermal properties of inorganic materials [6-7]. Semi-organic crystals have large damage threshold ,wide transparency range, excellent non-linear optical co-efficient, low angular sensitivity and exceptional mechanical properties [8- 15]. In the present work, Urea potassium chloride, a desirable semi-organic non-linear optical crystal, has been grown from aqueous solution using slow evaporation technique. In this article, we are reporting the growth, XRD, UV-Vis-NIR, photo conductivity, SEM, thermal analysis (TG-DTA), mechanical and dielectric property of the grown crystal.

2. Experimental procedure

2.1 Synthesis and crystal growth

Urea potassium chloride salt was synthesized using AR grade urea and potassium chloride in a stoichiometric ratio 2:1. The calculated amounts of salt were dissolved in Millipore water of resistance 18.2 MΩ cm at room temperature. The purity of the synthesized salt was further improved by successive recrystallization process. The grown crystal is as shown in Fig.1. A new semi-organic non-linear optical crystal of Urea Potassium Chloride (UPC) has been grown by slow evaporation technique. Good quality single crystal of size 9mm x 7mm x 5mm were obtained within 50 days.

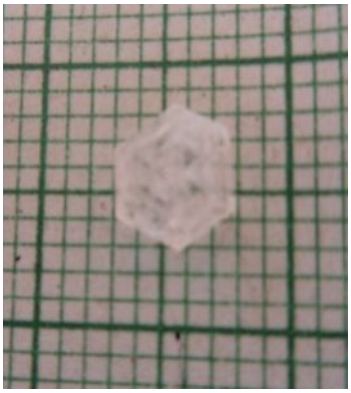


Fig.1.Photograph of UPC crystal

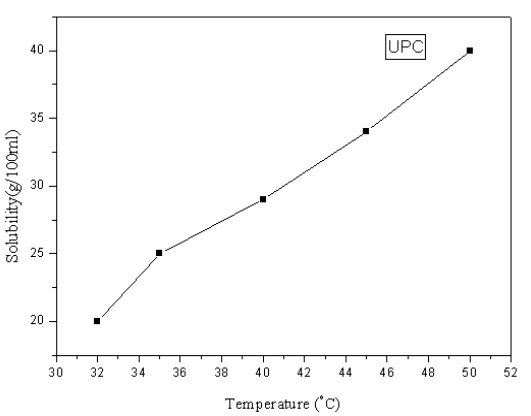


Fig.2. solubility curve of UPC crystal.

2.2 Solubility

The solubility studies of UPC were carried out for different temperature by gravimetric method using the solvent of water. The recrystallised salt of UPC was added in a small quantity to 100ml of Millipore at a constant temperature (32°C) with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute were analysed gravimetrically. This experiment was repeated for various temperatures 32, 35, 40, 45,50°C, and the solubility of UPC compound is shown in Fig.2. The solubility of UPC is relatively high in water when compared to ethanol, acetone.

3. Result and discussion

3.1 Single crystal XRD

The single crystal XRD analysis of UPC single crystal was carried out using Bruker Nonius CAD 4F single crystal diffractometer with MoK_α (λ=0.71073 Å) radiation. The structure was solved by direct technique and refined by the full matrix least square technique using SHELXL program. The crystal data are given in Table.1.

Table.1. Summary and details of UPC crystal

Empirical formula	$(CH_4N_2O)KCl$
Crystal color	Colourless, transparent
Size	9 x 7 x 5 mm^3
Crystal system	Cubic
Space group	Fm - 3c
Unit cell dimensions	a = b = c = 6.32 Å $\alpha = \beta = \gamma = 90^o$
Volume	252.43 $Å^3$
Diffractometer	Bruker Nonius CAD 4F
Radiation and wavelength	MoK_α(λ =.71703 Å)
Hygroscopicity	hygroscopic
UV – cutoff	220 nm

3.2 Powder X – ray diffraction analysis

X-ray diffraction technique is used to investigate the inner arrangement of atoms in a crystalline material. The grown UPC crystals were finely powdered and have been subjected to powder XRD analysis. All the observed reflections were indexed. The well defined Bragg's peak at specific 2θ angles shows high crystalline of UPC. The hkl values were indexed using the soft ware DICVOL. The indexed powder XRD pattern of the grown crystals is shown in Fig.3.

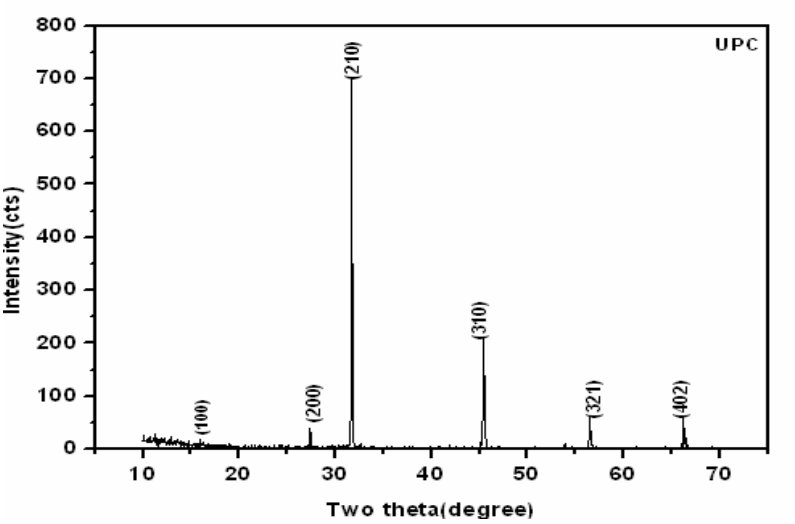


Fig.3. Powder X – ray diffraction pattern of UPC crystal.

3.3. FTIR analysis

In order to qualitatively analyze the presence of functional groups in the sample [16], the FTIR spectrum was recorded using a Perkin Elmer FTIR, Spectrometer by KBr pellet technique in the range 4000 – 500 cm^{-1} and the resultant spectrum is shown in the Fig.4. Frequencies of the fundamental vibration of UPC are listed in Table.2.

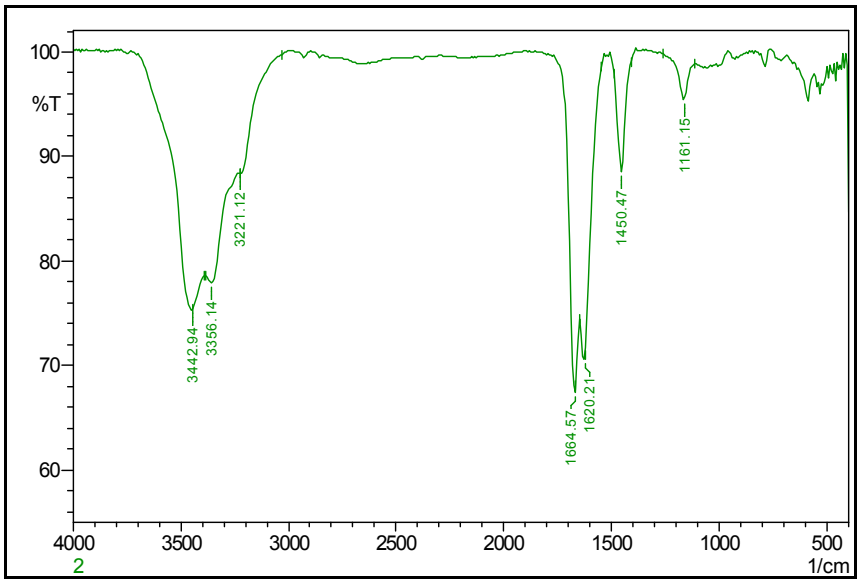


Fig.4. FT-IR Spectrum of UPC crystal.

Table .2. Frequencies of the fundamental vibration of UPC crystal.

Frequency in wave number(cm^{-1})	Assignment of vibrations
3442	NH2- Asymmetric stretching
3356	NH2- Symmetric stretching
3221	CH2- Stretching
3100	NH2- Symmetrical stretching
1664	NH2- Bending vibration
1620	C = O- Stretching vibration
1460	CH3- Symmetric bending vibration
1161	NH3- Rocking
800	C – C- Skeletal stretching
612	C – H- Deformation due to plane bending vibration
532	K - Cl- Stretching vibration

3.4. UV-Vis-NIR Spectral analysis

For studying optical transparency of the grown single crystals in the UV-Vis-NIR, an optical absorption spectrum was recorded in the wavelength range 200 – 800 nm using VARIAN CARY 5E Spectrophotometer. The obtained absorption spectrum is shown in Fig. **5.** The UV spectra show the presence of a wide transparency window lying between 220 nm and 800 nm with λ_{max} = 220 nm. The forbidden energy gap was estimated from the relation

$$E_g = \frac{1.243x10^3}{\lambda_{max}}$$

and E_g is found to be 5.65 eV, which is typical of dielectric materials.

As the crystal is colourless, its transmission is very high in the entire UV-Vis-NIR region. This is the most desirable property of the crystal used for NLO applications.

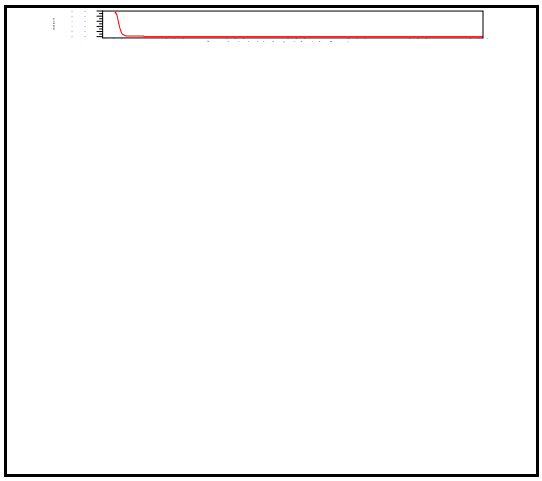


Fig.5.UV-Vis-NIR Spectrum of UPC crystal.

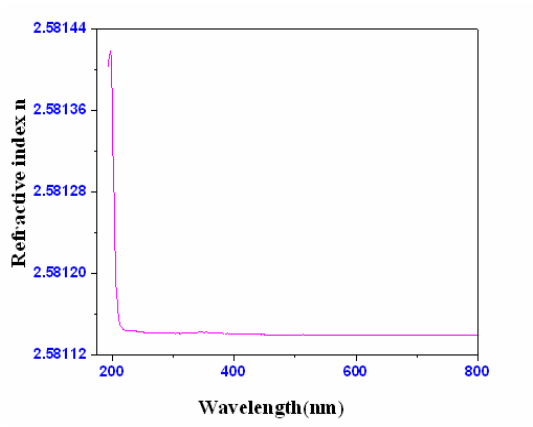


Fig. 6 Refractive index Vs wavelength of UPC

Calculation of optical constants.

The dependence of optical absorption coefficients with photon energy helps to study the band structure and the type of transition of the electron. The absorption coefficient (α) and the optical parameters such as refractive index (n), reflectance (R) and extinction coefficient (K) have been determined from the absorbance (A) spectrum based on the following relations:

$$\alpha = \frac{2.3026A}{t}$$

where A is the absorbance and t is the thickness of the crystal.

The relation between the optical band gap (Eg), absorption coefficient (α) and energy (hν) of the incident photon is given by

$$\alpha h\upsilon = B(h\upsilon - E_b)^r$$

where E_g is the optical energy gap of the crystal, B is a constant, h is the Planck's constant, ν is the frequency of incident photons and r is an index which can be assumed to have values of 1/2, 3/2, 2 or 3 depending on the nature of the electronic transition responsible for the absorption. r = ½ for allowed direct transition, r = 3/2 for forbidden direct transition and r = 3 for forbidden indirect transition, while r = 2 for indirect allowed transitions [17]. Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies

$$\alpha = \frac{(h\upsilon - E_g)^{1/2}}{h\upsilon}$$

The absorption coefficient 'α' is related to the extinction coefficient K by

$$K = \frac{\lambda\alpha}{4\pi}$$

where λ is the wavelength.

The absorption coefficient (α) and the extinction coefficient (K) were obtained from the transmittance (T) and reflectance (R) using the approximate formula

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)}$$

where t is the thickness of the sample.

The reflectance in terms of absorption coefficient can be obtained from the above relation [18]. Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T}$$

The refractive index n is obtained by using the reflectance data (R) given as

$$\backslash R = \frac{(n-1)^2}{(n+1)^2}$$

From the above two equations, the refractive index (n) can also be derived as

$$n = -\left[\frac{(R+1) \pm \sqrt{3R^2 10R - 3}}{2(R-1)}\right]$$

Fig. 6 depicts the wavelength dependence of the refractive index n. The refractive indices decrease monotonically when the wavelength increases for the sample. It also shows the presence of a wide transparency window lying between 240 nm and 1000 nm especially in the visible light region, which is consistent with the results of the optical absorption spectra in Fig. 5.

3.5. Thermal studies

Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) of UPC crystal was carried out between 20°C to 500°C at a heating rate of 20°C min^{-1} in nitrogen atmosphere is as shown in Fig.7. The initial mass of the material subjected to the analysis was 3.565mg and the final mass left out after the experiment was only 2.9% of the initial mass at a temperature of about 282°C indicating the bulk decomposition occurring in the sample. From the TG-DTA curves it is inferred that the decomposition of the materials takes place in the vicinity of 235.2°C. The sharpness of the endothermic peak at 191.3°C shows the good degree of crystallinity and purity of the sample. Further TG curve indicates no phase transition before 150.7°C and this enhances the temperature range for the utility of the crystal for NLO applications. There is a

gradual and significant weight loss as the temperature is increased above the melting point. From the thermal study, it can be conclude that the crystal is thermally stable up to 157.7°C.

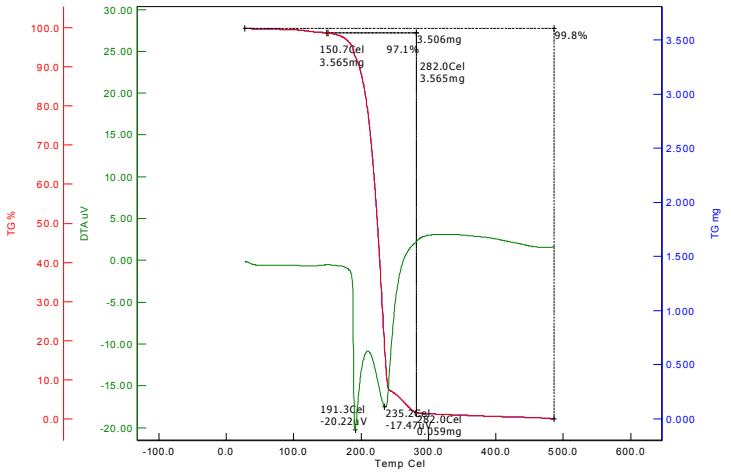
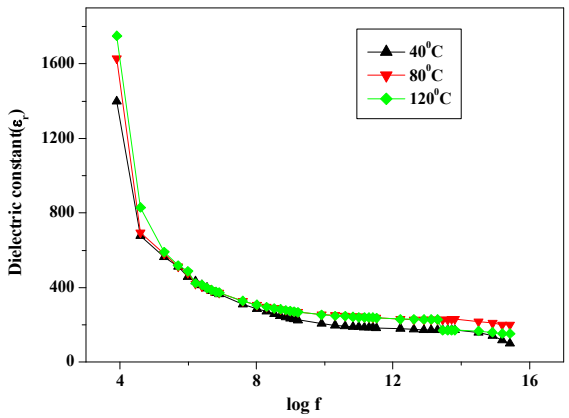


Fig.7. TG/DTA Spectrum of UPC crystal.

3.6 Dielectric studies

The dielectric study on UPC crystal was carried out by using the instrument, H10K1 3532-50 LCR HITESTER. A sample of dimension10 x 5 x 5 mm^3 having silver coating on the opposite faces was placed between the copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency from 50 HZ to 5 MHZ. Fig.8. Shows the plot of dielectric constant (ε_r) verses applied frequency.



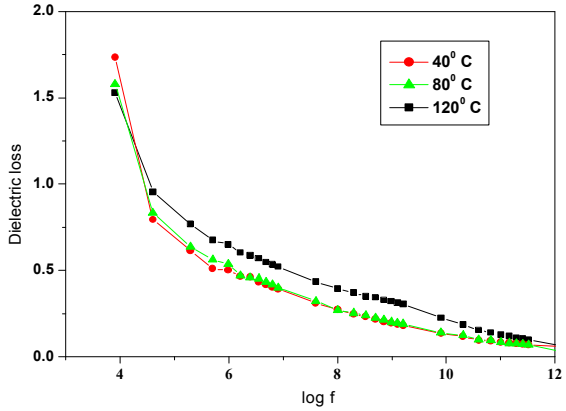


Fig.8.Variation of dielectric constant with log f **Fig.9.Variation of dielectric loss with log f**

The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency. The dielectric constant has a high value of 504 at 100 HZ and decreases to 113 at 5MHZ. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic , and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The dielectric constant is calculated using the relation $\varepsilon_r = Cd / A\varepsilon_0$. The variation of dielectric loss with frequency is shown in Fig.9.The characteristic of low dielectric loss with high frequency for a given sample suggests that the sample possess enhanced optical quality with lesser defect. Fig.10, and Fig.11.represents the variation of dielectric constant, dielectric loss with temperature.

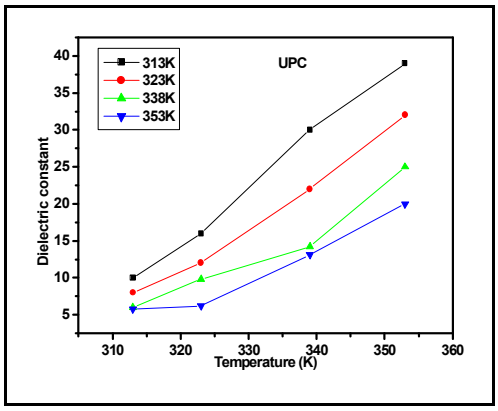


Fig.10. Variation of dielectric constant with temperature of UPC.

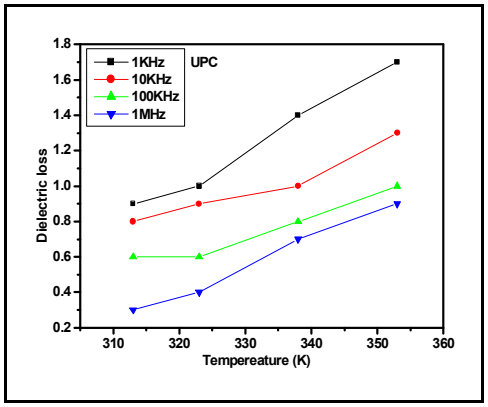


Fig.11. Variation of dielectric loss with temperature of UPC.

It is found that dielectric constant and dielectric loss values increase with increase in temperature, which correspond to a normal electrical behaviour. This can be understood on the mechanism of polarization. The electronic exchange of ions in the crystals gives rise to polarization. The low value of dielectric constant and dielectric loss at high frequencies are important for the materials in the construction of photonic and NLO devices.

3.7. Photoconductivity studies

Photoconductivity studies were carried out for the pure and doped LHA crystals using keithley 485 picoammeter at room temperature. By connecting the samples to a DC power supply and a picoammeter, dark conductivity of the samples were studied. The light from the halogen lamp (100 W) containing iodine vapour is focused on the respective samples with the help of a convex lens and the photo currents of the respective samples were measured [19]. The variation of both dark current (Id) and photo current (Ip) with applied field is shown in Fig. 12.

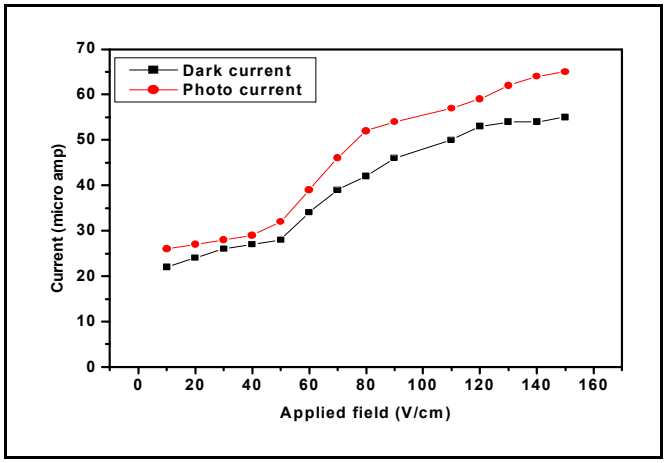


Fig.12. Field- dependent conductivity of UPC single crystal.

It is seen from the plots that both Id and Ip of the sample increase linearly with the applied field. Fig.11. shows the variation of both dark current and photo current with the applied field. From the graph both dark current and photo current varies with the applied field. It is further observed from the plot that the photocurrent is always greater than that of dark current, hence it can be concluded that UPC exhibits positive photoconductivity. This phenomenon can be attributed to generation of mobile charge carriers caused by the absorption of photons [20].

3.8. Vickers's Micro hardness Analysis

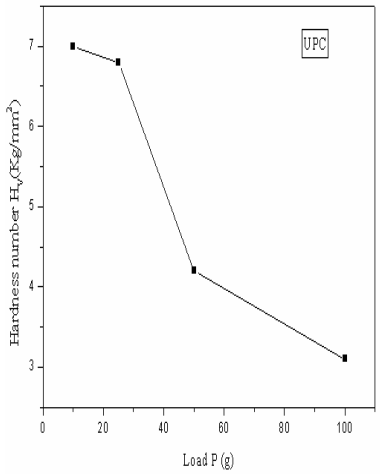


Fig.13. Variation of H_V with load

Hardness is an important solid state property, which is related to the bond strength on one hand and to the defect structure on the other hand. Hardness tests are commonly used to determine the structural and mechanical properties of the crystals. This test is a non-destructive one and will quickly yield quantitative information about the strength of the materials. The microhardness study was carried out on the as grown face (011) of the crystal Shimadzu HMV-2 Vickers indentation tester (Fig.13).

The hardness values H_v were calculated using the relation,

$H_v = 1.854 (P/d^2)$ kg/mm^2

Where H_V is Vickers hardness number, P- is the indentation load in kg and d is the diagonal length of the impression in mm. The micro hardness value was taken as the average of the several impression made. The maximum Vickers hardness value was measured to be 7 kg/mm^2. The value of n comes out to be 1–1.6 for hard materials and more than 1.6 for soft ones [21]. Thus, the present crystal under study belongs to soft material category.

3.9. Scanning Electron Microscope

An ordered morphology of crystal surface is an essential requirement for linear and non linear applications. Crystals without imperfections like non flatness, misorientation, in homogeneity shows good NLO behaviour. The recorded SEM image of UPC crystal with 5µm focusing is shown in Fig.14. The magnification of SEM was about 150 times. The sample was kept in high vacuum with an accelerating voltage of 10kV. From the figure it is clear that the crystal possesses almost smooth surface, few valley regions and free from cracks. However very few micro crystals are seen on the surface.

Table.3. Comparative efficiency of UPC crystal.

Crystal	Input power	Output power	Efficiency
KDP crystal	6.9 mJ	7.2 mV	1.0
UPC crystal	6.9 mJ	9.2mV	1.3

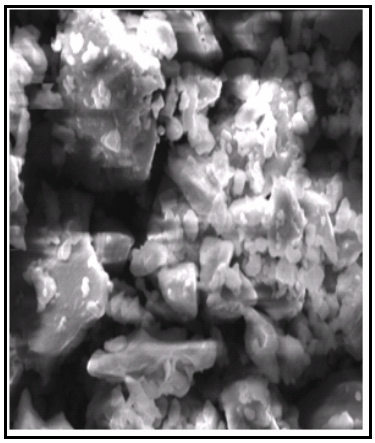


Fig.14. SEM image of UPC crystal

3.7 . Nonlinear optical studies

The non linear property of the grown UPC crystal were tested by passing the output of Nd : YAG laser beam of wavelength 1064nm, generating about 6mJ/pulse. This laser can be operated in two modes. In the single shot mode, the laser emits a single 8 ns pulse. In the multi shot mode, the laser produces a continuous train of 8 ns laser pulse at a repetition rate of 10 Hz. In the present study, the single shot mode of 8ns pulse with a spot radius of 1mm was used. The experimental set up used a mirror and 50/50 beam splitter, to generate a beam with pulse energy of 6mJ. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample was detected by photodiode detector and oscilloscope assembly. The SHG efficiency in the UPC crystal was evaluated by the Kurtz and Perry powder technique [22] and microcrystalline powder of KDP was taken as the reference material. It is found that the frequency doubling efficiency of the UPC crystal is 1.3 times than that of KDP crystal. The comparative efficiency is shown in Table.3.

4. Conclusion

Colourless, transparent crystal of Urea Potassium Chloride was conveniently grown by slow evaporation method. The XRD analysis confirms the crystalline nature of the materials and lattice parameters. The presence of various functional groups present in the UPC crystals has been confirmed by FTIR analysis. The UV–Vis–NIR absorption spectrum shows that the cut-off wavelength is around 220 nm with energy band gap of 5.179 eV. UV–Vis–NIR absorption spectrum and wavelength dependence of refractive index confirms the wide transparency window lying between 220 nm and 800 nm. The TGA/DTA studies ascertain the thermal stability of the sample up to 157^0 C. It is found that both dielectric constant and loss decrease with increase in frequency. Photoconductivity studies reveal that the UPC exhibits positive photoconductivity. Mechanical strength of the material was calculated using Vickers microhardness and it was found that the material belongs to soft materials category. The SHG efficiency of the grown UPC crystal was 1.3 times greater than the KDP crystals. Owing to all these properties UPC could be a promising material for NLO applications.

5. References

1. Rajasekaran .R., Ushasree P.M., Jayavel R., Ramasamy P.,Growth and characterization of zinc thiourea chloride(ZTC) a semiorganic nonlinear optical crystal., J. Cryst Growth, (2001) 229,563-567.
2. Jaikumar.D.,Kalainathan.S.Bhagavanarayanan.G.,Structural,Spectral, Thermal, Dielectric, Mechanical and Optical properties of Urea L-alanine acetate single crystals.,Physica B, (2010) 405, 2394-2400.
3. Goma.V., Padma.C.M and Mahadevan.C.K., Dielectric parameters of KDP single crystals added with urea., Matt.Lett, (2006) 60, 3701-3705.
4. Chidambaram.,V., Jerome das .S., Arivudai nambi.R., Krishnan.s., Synthesis, growth and characterization of non linear optical urea-ammonium chloride crystal., Solid state sciences , (2012) 14, 216-218.
5. Krishnamurthy.R., Rajasekaran.R., Bincy susan Samuel., Growth and characterization of KDP crystal doped with l- aspartic acid, (2013) 104, 310-314.

6. Balamurugan, N., M.Lenin, G. Bhagavannarayana and P. Ramasamy, Growth of TGS crystal using uniaxially solution-crystallization method of sankaranayanan- Ramasamy, Cryst. Res. Technol, (2007) 42, 151-156.
7. Donaldson.W.R. and Tang.C.L. Urea optical parametric oscillator, Appl. Phys.Lett, (1984) 44, 25-27.
8. Ushasree,P.M.,Muralidharan,R., Jayavel,R., Ramasamy, P., Growth of bis thiourea Cadmium chloride single crystals a potential NLO material of organometallic complex, J. Cryst.Growth, (2000) 218, 365-371.
9. Krishnamurthy.R., Rajasekaran.R., Bincy susan Samuel., Growth and characterization of KDP crystal doped with l- aspartic acid, (2013) 104, 310-314.
10. Selvam A., Pandi S., Selvakumar S. and Srinivasan S., Growth and characterization of urea citric acid(UCA) single crystal by slow evaporation process, J. Appl. Sci. Res., (2012) 4, 2474- 2478.
11. Anie Roshan, S., Cyriac Joseph, Ittyachen, M.A. "Growth and Characterization of a new metal-organic crystal: Potassium thiourea bromide" Mater. Lett (2001) 49, 299-302.
12. Balamurugan, N., Lenin, M. and Ramasamy, P. "Growth of potassium acid phthalate crystals by Sankaranarayanan-Ramasamy (SR) method and its optical characterization" Mater. Lett., (2007) 61,1896-1898.
13. Ilango.E, Rajasekaran.R, Shankar.K, Chidambaram.V..Synthesis, Growth and characterization of non linear optical Bisthiourea Ammonium Chloride single crystals by slow evaporation technique, Optical materials, (2014) 37, 666-670.
14. Joshi, M.S. and and Antony A.V. "The kinetics of potassium dihydrogen phosphate crystal growth from aqueous solution" J. Phys D: Appl. Phys, (1977) 10, 2393-2396.
15. Mullin, J.W. and Amatavivadhana, A, "Growth kinetics of ammonium and potassium dihydrogen phosphate crystals" J. Appl. Chem, 17, (1967) 151-156.
16. Nakamoto.K., IR Spectra of Organic and Inorganic and coordination compounds 2nd Ed, Wiley, New York. (1978).
17. G. R. Dillip, G. Bhagavannarayana, P. Raghavaiah and B. Deva Prasad Rajud, Mater. Chem. Phys., 2012, 134, 371.
18. S. Suresh, J. Cryst. Process Technol., 2013, 3, 87.
19. F. Xavier, A. Regis Inigo, G. Goldsmith, A. Porphyrines, Phthalocyanines 3 (679) (1999).
20. V.N. Joshi, Photoconductivity, Marcel Dekker, New York, 1990.
21. Shakir M, Ganesh V, Wahab MA, Bhagavannarayana G, Kishan Rao K. Structural, optical and mechanical studies on pure and Mn^{2+} doped L-asparagine monohydrate single crystals. Mater Sci Eng B. 2010;76:470–5.
22. Kurtz, S. K. Perry, T. T., "A Powder Technique for the Evaluation of Nonlinear Optical Materials" J. Appl. phys. 39, (1978) 3798-4013.

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