Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

XRD, Optical, Mechanical and Dielectric Studies of Sodium Sulfate Doped Tetrakis -Thiourea Potassium Chloride Crystals

J.Jude Brillin[1] and P.Selvarajan[2*]

[1]Research scholar, Manonmaniam Sundaranar University, Abishekapatti-627 012, Tirunelveli, Tamilnadu, India.
[2]Department of Physics, Aditanar college of Arts and science, Tiruchendur-628216, Tamilnadu, India.

ABSTRACT

Undoped tetrakis-thiourea potassium chloride (TTPC) and sodium sulfate doped TTPC crystals were grown by solution method with slow evaporation technique at room temperature. The grown crystals were colourless and transparent. The solubility of the grown samples has been found out at various temperatures. The lattice parameters of the grown crystals were determined by the single crystal X-ray diffraction technique. UV-visible transmittance studies were carried out for the grown samples and linear optical constants were evaluated. Nonlinear optical studies reveal that the SHG efficiency is increased when TTPC crystal is doped with sodium sulfate. From microhardness studies, it is observed that sodium sulfate doped TTPC crystal is more harder than the undoped crystal. The dielectric constant and loss factor of the samples were estimated at different frequencies and temperatures and the results are analysed.

Key words : Crystal growth; doping; Characterization; XRD ; NLO; Hardness; Dielectric constant; Optical transmittance;SHG

***Corresponding author**

P. Selvarajan

Department of Physics,

Aditanar college of Arts and science,

Tiruchendur-628216, Tamilnadu, India.

Email: pselvarajanphy@yahoo.co.in

Mobile: 08870428536

1. INTRODUCTION

Nonlinear optical (NLO) materials have potential applications in second harmonic generation (SHG), optical computing, optical communication, photonics, electro-optic modulation, optical parametric amplification, optical image processing etc[1,2,3] NLO materials are classified into organic, inorganic, semiorganic and polymer NLO materials. A semiorganic NLO crystal is a combination of organic and inorganic materials. In this work, the semiorganic NLO crystals viz., undoped tetrakis-thiourea potassium chloride (TTPC) and sodium sulfate doped TTPC crystals are prepared and characterized. In recent years, a number of semiorganic complex products of thiourea have attracted great interest because these metal–organic complexes combine the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics[4,5,6,7,8]. Azhar *et al.* reported recently the growth and various studies of potassium thiourea chloride crystal and here the laser damage threshold (LDT) value of potassium thiourea chloride crystal has been determined by pulse multi shot method using the Nd:YAG laser operating at 1064 nm and the third order nonlinear optical nature of grown crystal has been investigated at 632.8 nm employing the He-Ne laser assisted Z-scan studies[9]. A comparative characterization study of pure and glycine doped potassium thiourea chloride crystal for laser frequency conversion applications was reported in the literature[10]. Another important thiourea metal complex viz., potassium thiourea bromide was studied and dopants like manganese and vanadium were added into potassium thiourea bromide to alter its properties[11,12,13]. It has been reported in the literature that doping NLO crystals with various dopants can alter physical and chemical properties and doped NLO crystals find wide NLO applications compared to undoped NLO crystals[14,15] . Hence, the aim of this paper is to report the results of growth and study of the undoped and sodium sulfate doped TTPC crystals.

2. EXPERIMENTAL

2.1 Synthesis and solubility

The compound tetrakis-thiourea potassium chloride (TTPC) was synthesized by taking the precursor chemicals like AR grade thiourea and AR grade potassium chloride in the molar ratio of 4:1. The calculated reactants were dissolved in double distilled water and stirred well using a magnetic stirrer for about 3 hours. The solution was heated at 60 ^{o}C until the synthesized salt of TTPC was obtained. The purity of the synthesized salt was improved by repeated re-crystallization. To get the sodium sulfate doped TTPC, 1 mole% of sodium sulfate was added to aqueous solution of TTPC. Solubility study was carried out for the twice re-crystallized TTPC salt in double distilled water by gravimetrical method[16]. A glass beaker with 25 ml of double distilled water was placed inside a constant temperature bath (accuracy : $\pm$ 0.01^{o}C), maintained at 30°C. The sample of TTPC was added in small amounts at successive stages. The addition of the salt and the stirring were continued till a small precipitate was formed, which confirmed the supersaturated condition. Then 5 ml of the saturated solution was pipetted out and poured into a petri dish of known weight. The solvent was completely evaporated by warming the solution at 50°C. The amount of the salt present in 5 ml of the solution was measured by subtracting the weight of the empty petri dish. From this, the amount of the salt present in 100 ml of the solution was calculated. In the same manner, the amount of the salt dissolved in 100 ml at 35, 40, 45 and 50°C was determined. The same procedure was followed to find solubility of potassium sulfate doped TTPC sample at various temperatures. The solubility diagram for pure and sodium sulfate doped TTPC samples are shown in figure 1. It is observed that solubility increases with temperature for both the samples. Since solubility increases with temperature, the samples of this work have positive temperature coefficient of solubility.

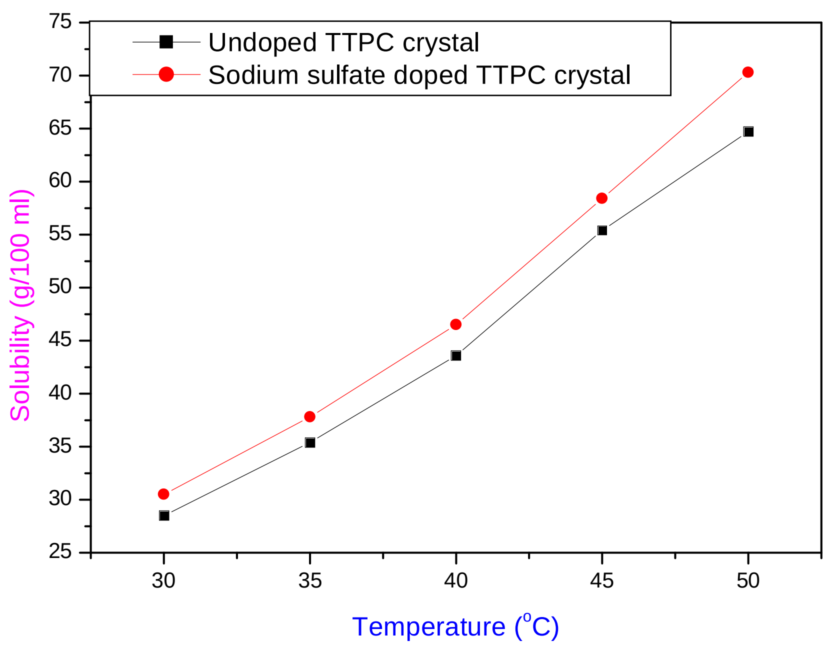


Fig.1. Solubility curves for undoped and sodium sulfate doped TTPC crystals

2.2. Growth of sample crystals

Using the solubility data, saturated solution of TTPC was prepared. Single crystals of TTPC were grown from the aqueous solution using slow evaporation method. The solvent was allowed to evaporate and initially tiny crystals were formed at the bottom of the container due to spontaneous nucleation. To obtain a big-sized crystal of TTPC, seed immersion technique was adopted. Transparent and colourless crystal was obtained after a period of about 30 days. For the growth of the doped crystal, the synthesized salt of sodium sulfate doped TTPC was used to prepare the saturated solution and by slow evaporation, the sample crystals were harvested. The photograph of the grown crystals of pure and sodium sulfate doped TTPC is presented in figure 2. The morphology of sodium sulfate doped TTPC crystal is seen to be different when compared to the undoped TTPC crystal.

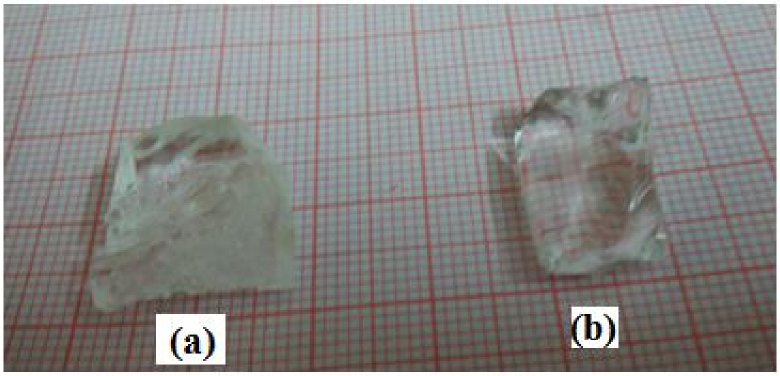


Fig. 2. Photograph of (a) undoped TTPC and (b) sodium sulfate doped TTPC crystals

3. RESULTS AND DISCUSSION

3.1 Single crystal XRD studies

Single crystal XRD data of undoped TTPC and sodium sulfate doped TTPC crystals were collected using ENRAF CAD-4 X-ray diffractometer with MoK_{α} λ=0.71069 Å) radiation and the obtained data are given in the table 1. From the results, it is observed that both the grown crystals crystallize in tetragonal system with the space group $P4_1$. The unit cell parameters of pure TTPC crystal obtained in this work are observed to be in close agreement with reported work[17] and slight change of lattice parameters is observed for the sodium sulfate doped sample compared to undoped TTPC crystal. The changes in the lattice parameters may be attributed to the presence of sodium sulfate in the lattice of TTPC crystal. The presence of dopant in TTPC crystal may produce lattice strain which leads to change of unit cell parameters in the host TTPC doped sample.

Table 1. Single crystal XRD data for undoped and sodium sulfate doped TTPC crystals

Crystal parameters	Undoped TTPC crystal	Sodium sulfate doped TTPC crystal
a (Å)	20.478 (4)	20.497(2)
b (Å)	20.478(5)	20.497(2)
c (Å)	8.531(3)	8.536(4)
□	90°	90°
□	90°	90°
□	90°	90°
Crystal system	Tetragonal	Tetragonal
Space group	$P4_1$	$P4_1$
Volume of unit cell	3577.46(2) $Å^3$	3586.21(4) $Å^3$

3.2. Estimation of transmittance, absorption coefficient and optical band gap

UV-visible transmittance spectra of undoped TTPC and sodium sulfate doped TTPC crystals were recorded using a UV-visible spectrophotometer in the wavelength region 190-1100 nm and the spectra are presented in the figure 3. The UV lower cut-off wavelength is observed to be at 238 nm for both the samples. It is found that the percentage of transmission has been slightly increased in the case of sodium sulfate doped TTPC crystal. The sharp fall at 238 nm for both the samples corresponds to fundamental absorption edge which is essential in connection with the theory of band theory of solids. The increase in the transmittance for the sodium sulfate doped TTPC crystal seems to be due to the presence of dopants in the doped crystal. The measured transmittance (T) is used to calculate the absorption coefficient (α) using the relation □□= $[2.303 \log_{10} (1/T)] / d$ where T is the transmittance and d is the thickness of the crystal. The plots of absorption coefficient versus the wavelength for the samples are shown in the figure 4. From these plots, it is noticed that the absorption coefficient values are low in visible region and very high at the cut-off wavelength. Near the absorption edge, the value of absorption coefficient increases rapidly with wavelength. The values of aborption coefficient of sodium sulfate doped TTPC crystal are found to be low compared to that of undoped TTPC crystal.

Optical absorption coefficient (α) follows the Tauc's equation and it is given below.

$$\alpha h\nu = A\sqrt{(h\nu - E_g)}$$

where E_g is the optical band gap energy of the crystal, h is the Planck's constant, ν is the frequency of the light and A is a constant[18]. The Tauc's plots were plotted between $(\alpha h\upsilon)^2$ with the optical energy ($h\upsilon$) are shown in figure 5 (a) and (b) for undoped and sodium sulfate doped TTPC crystals. The band gap energy is found to be 5.22 eV for both the samples. In a crystalline material, either direct or indirect optical transitions are possible depending on the band structure of the material. There will be a single linear region in direct transition and two linear portions in indirect transition. For a direct transition, the plot of $(\alpha h\upsilon)^2$ and ($h\upsilon$) is taken into account and for the indirect trasition, the plot of $(\alpha h\upsilon)^{1/2}$ and ($h\upsilon$) is considered. The single linear portions in figures 5 (a) and 5(b) indicate that both the samples belong to the direct band gap materials[19,20].

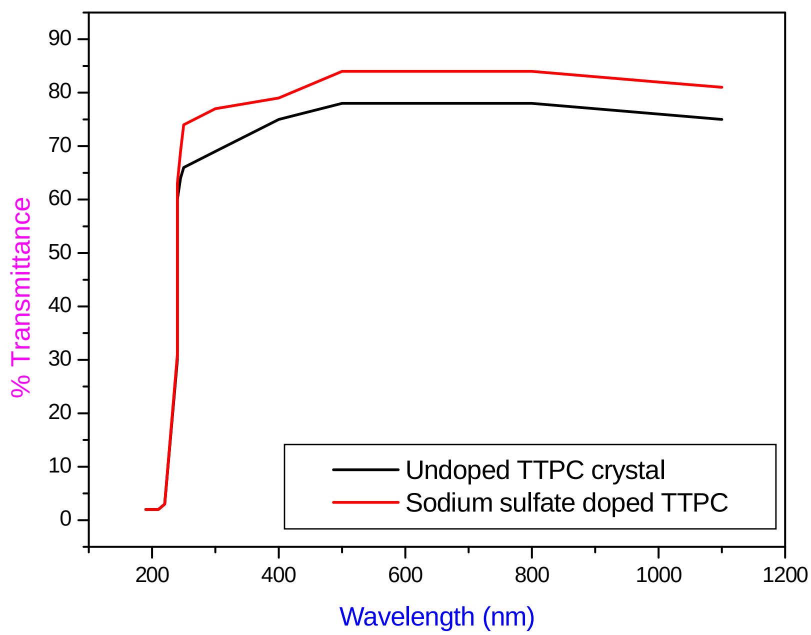


Fig.3. Plots of transmittance versus wavelength for undoped and sodium sulfate doped TTPC crystals

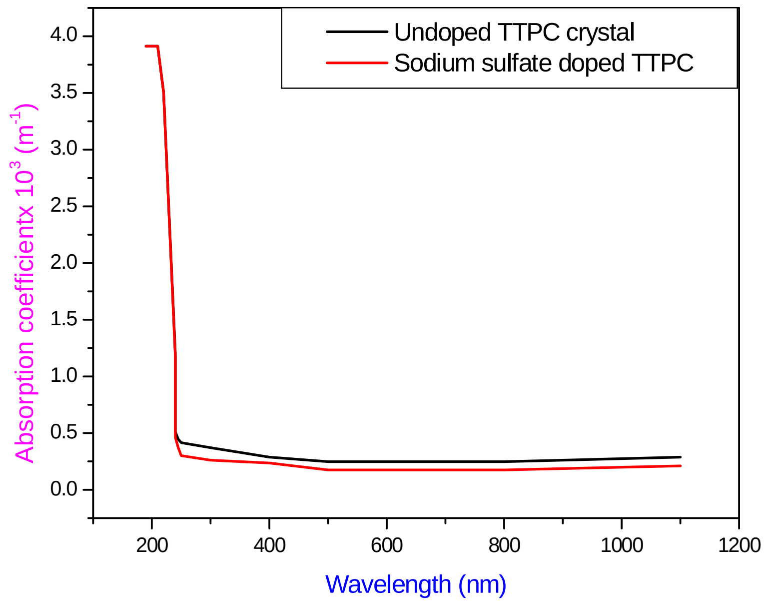
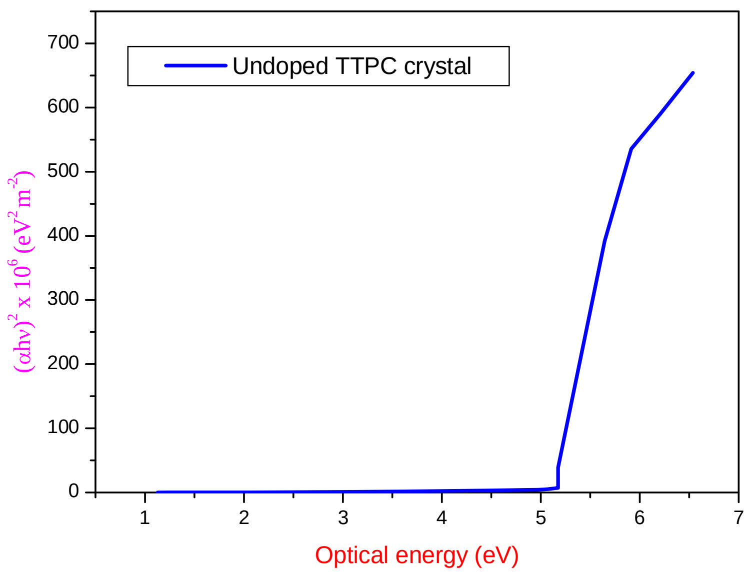
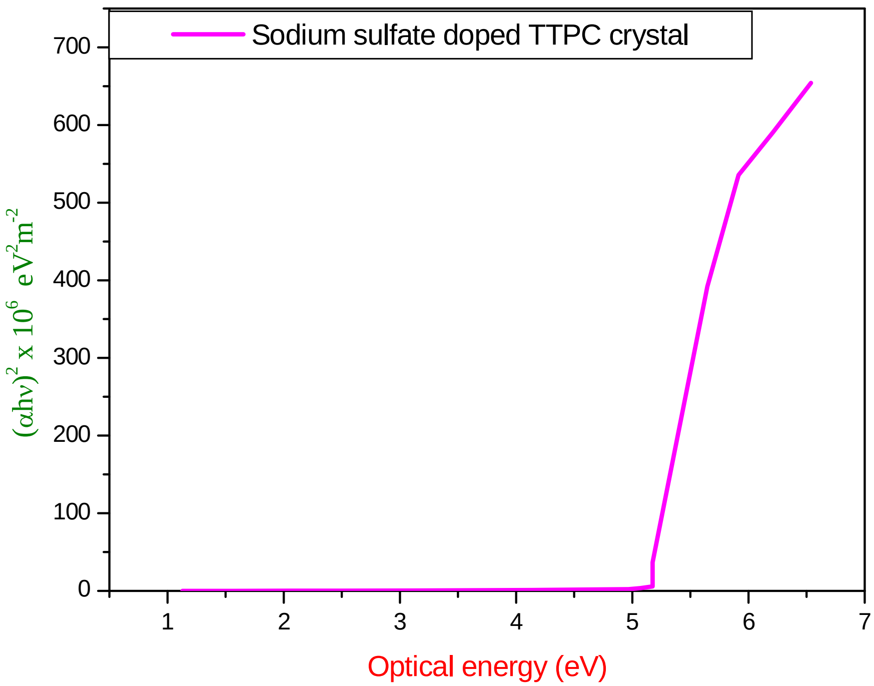


Fig.4. Plots of absorption coefficient versus wavelength for undoped and sodium sulfate doped TTPC crystals



(a)



(b) **Fig.5. Tauc's plots for (a) undoped and (b) sodium sulfate doped TTPC crystals**

3.3 Measurement of SHG efficiency

The second harmonic generation (SHG) efficiency of undoped and sodium sulfate doped TTPC samples was measured by powder Kurtz and Perry technique[21]. The crystal was grounded into a homogenous powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser beam of wavelength 1064 nm (pulse width 6 ns) was allowed to strike the sample cell normally. The SHG output of wavelength 532 nm was finally detected using a photomultiplier tube. A sample of powdered potassium dihydrogen phosphate (KDP) was used as the reference material in the SHG measurement. The obtained data in connection with SHG measurement are given in the table 2. From the data, the relative SHG efficiency of undoped TTPC crystal is 0.95 times that of the reference KDP sample and the relative SHG efficiency of sodium sulfate doped TTPC crystal is 1.36 times that of the reference KDP sample. Hence, the sodium sulfate doped TTPC crystal is the better candidate for second order NLO applications.

Table 2. Relevant data for the samples from SHG measurement

S. No.	Sample name	Output energy (milli joule)	Input energy (joule)	Relative SHG efficiency
1	Undoped TTPC	8.46	0.70	0.95
2	TTPC + 1 mole% of sodium sulfate	12.11	0.70	1.36
3	KDP (Reference sample)	8.91	0.70	1

3.4 Microhardness, work hardening coefficient and yield strength

The grown crystals of the undoped and sodium sulfate doped TTPC crystals with flat and smooth faces were selected for microhardness studies. Indentations were made using a Vickers microhardness tester on the selected crystal. The flat surface of the selected crystal was polished gently with ethanol–water mixture before carrying out the indentation study. The crystal was mounted properly on the base of the microscope and the selected face was indented by the loads 25 g, 50 g, 50 g and 100 g for period of 15 seconds using Vickers diamond pyramidal indenter attached to a microscope. The average diagonal indentation length was measured by a calibrated micrometer attached to the eye piece of the microscope after unloading and the average (d) is obtained. The microhardness of the crystals is determined using the relation $H_v = 1.8544\ P/d^2$ where H is the Vickers hardness number, P is the indentation load and d is the average diagonal length of the impression in mm. The variation of microhardness number with the applied load for undoped TTPC and sodium sulfate doped TTPC crystals is presented in the figure 6. The hardness increases gradually with the increase of load and above 100 g, cracks develop on the smooth surface of the crystal due to release of the internal stresses generated locally by indentation. This can be explained qualitatively on the basis of depth of penetration of the indenter. For small loads, only a few surface layers are penetrated by the indenter. The measured hardness is the characteristics of these layers and hardness increases with load. With increase in load, the overall effect is due to surface as well as inner layer of the sample. Due to reverse indentation size effect, the hardness increases with increase of the applied load[22,23,24]. From the results, it is observed that the hardness of TTPC crystal increases when it is doped with sodium sulfate. The addition of sodium sulfate into TTPC crystal probably enhances the strength of bonding in the host material and hence hardness number increases.

Meyer's law is given by $P=a\ d^n$ where P is the applied load, d is average diagonal indentation length, n is the work hardening coefficient and a is a constant. This equation can be written as log P = log a + n log d and a plot of log P versus log d can be drawn and the slope can be obtained. The slope is equal to the Meyer's index number or work hardening coefficient[25]. Plots of log P versus log d for the samples are displayed in the figures 7 and 8. The obtained values of work hardening coefficient are 2.296 and 2.752 respectively for undoped and sodium sulfate doped TTPC crystals. As the values of work hardening coefficient of the samples are more than 1.6, the samples are confirmed as the soft materials[26]. Yield strength is one of the mechanical parameters like hardness and it depends on both hardness value (H_v) and the work hardening coefficient (n). Since n is found to be more than 2, yield strength (σ_y) of the crystal can be found out using the relation $\sigma_y = (H_v/3)(0.1)^{n-2}$. The evaluated values of yield strength for the samples are given in the table 3. From the results, it is observed that the yield strength values increase with the applied load for both undoped and sodium sulfate doped TTPC crystals. Since the value of work hardening coefficient of sodium sulfate doped TTPC crystal is slightly more than that of undoped TTPC crystal, the estimated values of yield strength of doped TTPC crystal is observed to be less than compared that of undoped TTPC crystal[27,28].

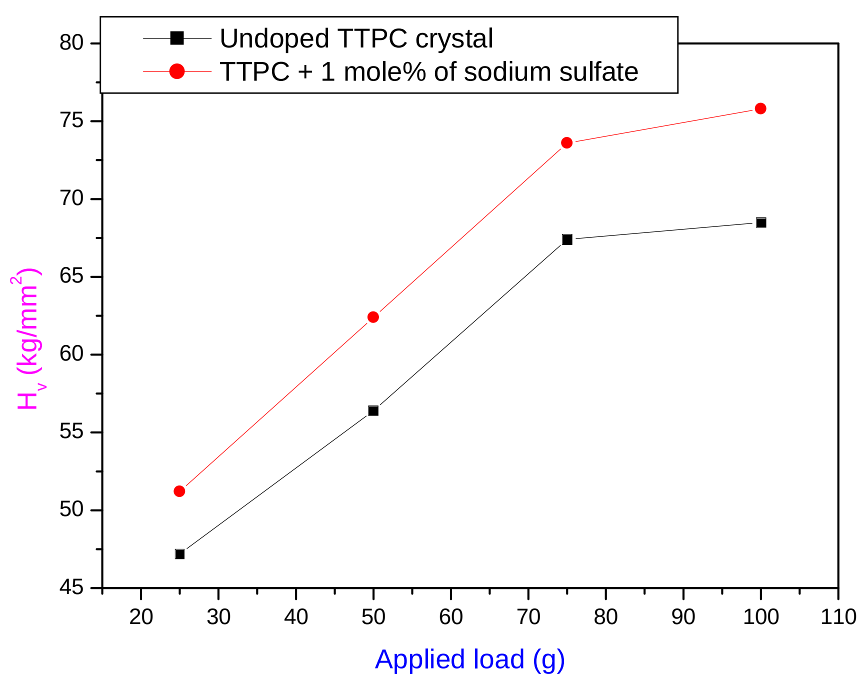


Fig.6. Variation of hardness number with the applied load for undoped and sodium sulfate doped TTPC crystals

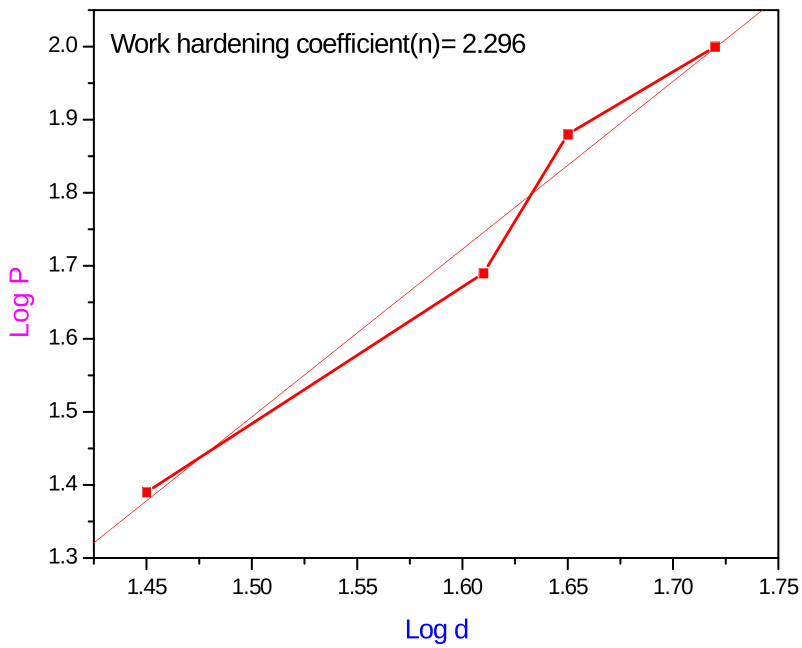


Fig.7. Variation of log P versus log d for undoped TTPC crystal

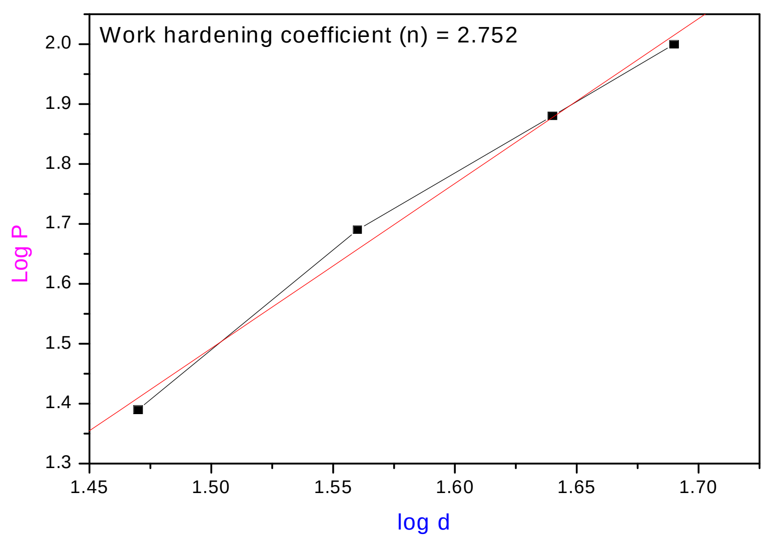


Fig.8. Variation of log P versus log d for sodium sulfate doped TTPC crystal

Table 3. Estimated values of yield strength for undoped and sodium sulfate doped TTPC crystals

S.No.	Applied load (grams)	Yield strength x 10^6 (pascal)	
		Undoped TTPC Crystal	Sodium sulfate doped TTPC crystal
1.	25	77.98	29.60
2.	50	93.19	36.11
3.	75	110.36	42.56
4.	100	113.12	43.83

3.5. Dielectric Characterization

The dielectric constant and loss factor of undoped and sodium sulfate doped TTPC crystals were measured using the parallel plate capacitor method at various temperatures ranging from 30 to 80 ^{o}C using an Agilent 4284A LCR meter at different frequencies ranging from 10^2 to 10^6 Hz. Opposite faces of the sample crystal were coated with good quality silver paste to obtain a good conducting surface layer. The accuracy in measuring dielectric constant and dielectric loss factor is 2% and 5% respectively. The variations of dielectric constant and dielectric loss factor as a function of frequency at different temperatures are presented in the figures 9-12. The dielectric parameters are found to be decreasing with increasing of frequency and are found to be increasing with increase of temperature. This can be explained on the basis of polarization and conduction processes which are involved when electric field is applied to the samples. The electronic exchange of the number of ions in the sample gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. The nature of decrease of dielectric constant and dielectric loss with frequency suggests that the crystals of this work seem to contain dipoles of continuously varying relaxation times. Since the dipoles of larger relaxation times are not able to respond to the higher frequencies, the dielectric constant and loss tangent are low at higher frequencies. Low value of dielectric loss indicates that the grown undoped and sodium sulfate doped TTPC crystals are good quality dielectric materials with less number defects. From the results, it is observed that TTPC crystals are doped with sodium sulfate, the dielectric constant and loss factor are found to be increasing. The increase in dielectric constant with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The increase at higher temperatures is mainly attributed to the thermally generated charge carriers and impurity dipoles. The nature of variations of dielectric constant with frequency and temperature indicates the type of contributions that are present in them[29,30,31].

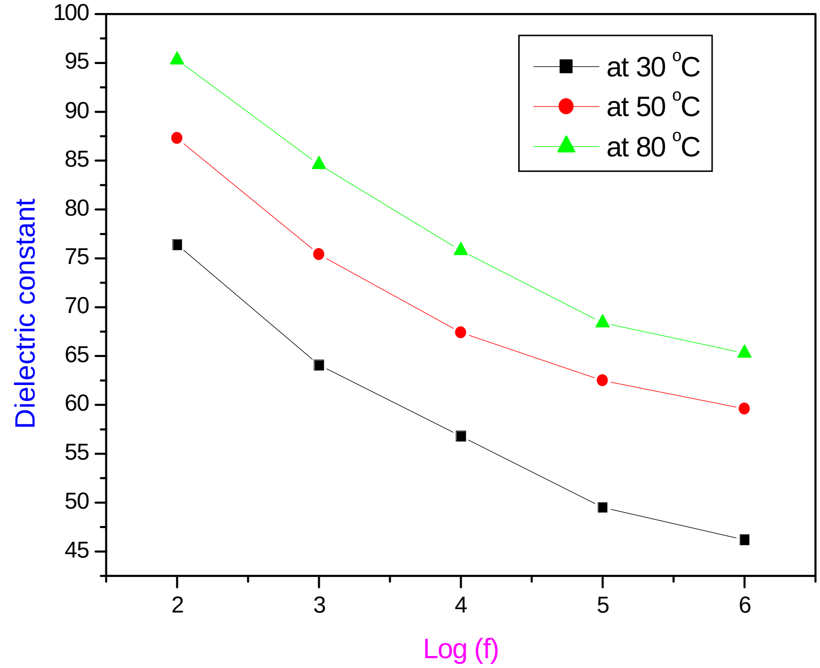


Fig.9. Variation of dielectric constant with frequency for undoped TTPC crystal at different temperatures

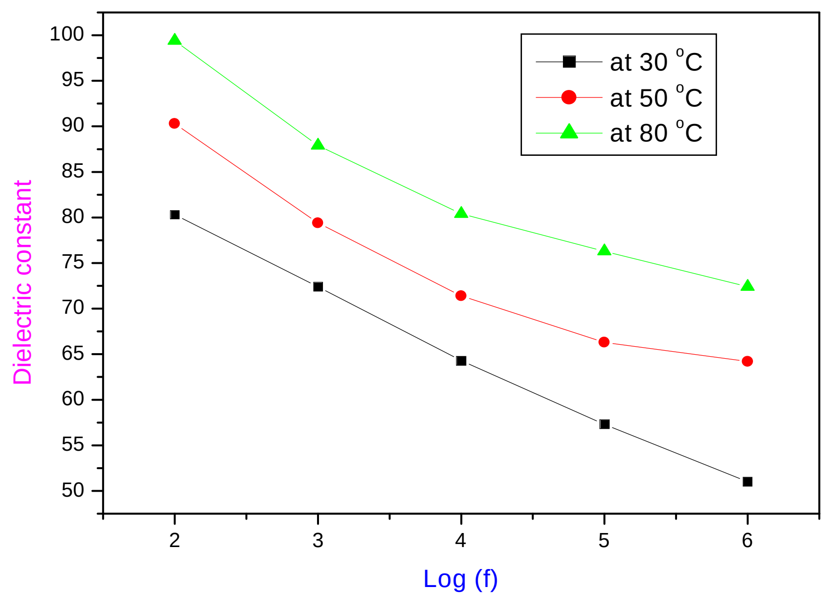


Fig.10. Variation of dielectric constant with frequency for sodium sulfate doped TTPC crystal at different temperatures

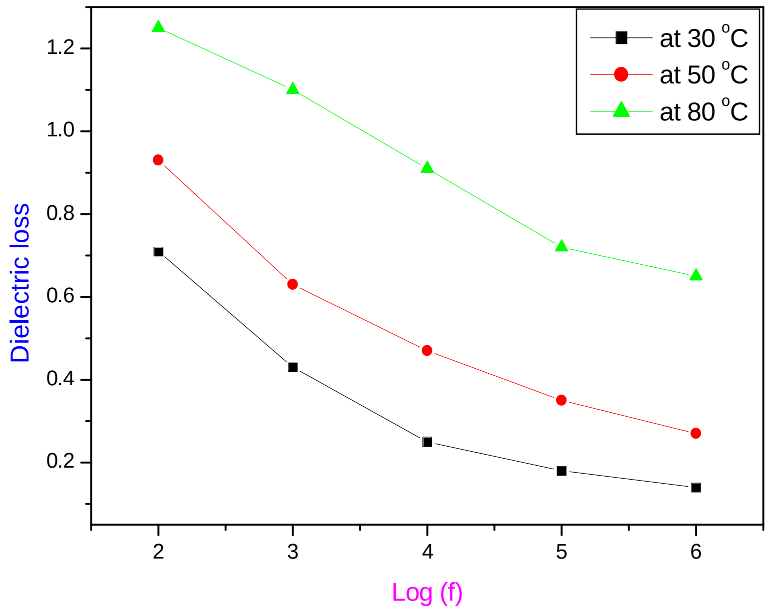


Fig.11: Variation of dielectric loss with frequency for undoped TTPC crystal at different temperatures

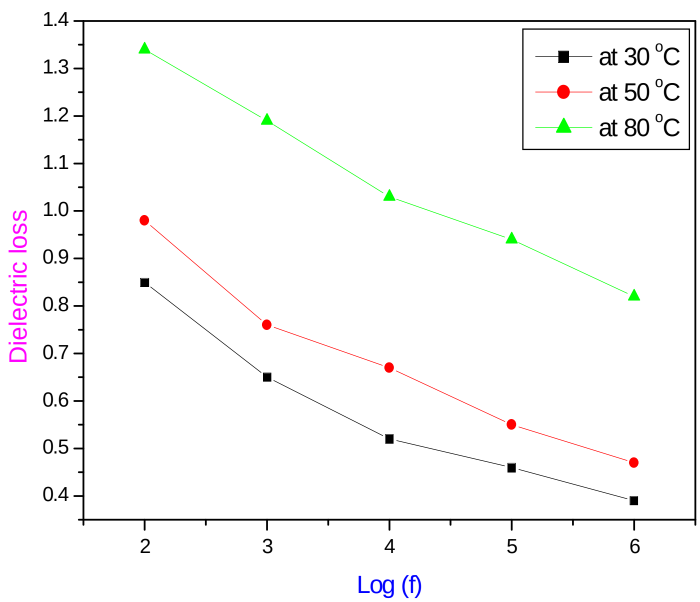


Fig.12: Variation of dielectric loss with frequency for sodium sulfate doped TTPC crystal at different temperatures

4. CONCLUSIONS

Solution method was adopted to synthesize the undoped and sodium sulfate doped tetrakis-thiourea potassium chloride salts and single crystals of the samples were prepared by slow evaporation technique. Solubility studies were carried out for the samples in water at different temperatures. XRD studies reveal that the grown crystals crystallize in tetragonal crystal system. The optical transmittance, absorption coefficient and band gap of the samples were estimated. The optical band gap of the samples was obtained from Tauc's plots. The SHG efficiency of sodium sulfate doped TTPC crystal is found to be more than that of undoped TTPC crystal. The mechanical parameters such as hardness, yield strength and work hardening coefficient of the samples have been evaluated. The dielectric parameters of sodium sulfate doped TTPC crystal are observed to be more than those of undoped TTPC crystal and this is due to incorporation of sodium sulfate in the form of ions in the interstitial positions of the host TTPC crystals.

ACKNOWLEDGEMENTS

The authors are grateful to staff members of Crescent Engineering College (Chennai), St.Joseph's College (Trichy), SAIF, Cochin University for the research supports given to carry out this work. We also thank authorities of the management of Aditanar College of Arts and Science, Tiruchendur and M.S. University, Tirunelveli l for the encouragement given to us to carry out the research work.

REFERENCES

1. Meera K, Muralidharan R, Dhanasekaran R, Prapun Manyum, Ramasamy P. Growth of nonlinear optical material: L-arginine hydrochloride and its characterization. J.Crystal Growth. 2004; 263: 510 -517.
2. Vimalan M, Ramanand A, P.Sagayaraj P. Synthesis, growth and characterization of l-alaninium oxalate crystals. Cryst.Res. Technol. 2007; 42:1091-1095.
3. Kirubavathi K, Selvaraju K, Valluvan R, Vijayan N, Kumararaman S. Synthesis, growth, structural, spectroscopic and optical studies of a new semiorganic nonlinear optical crystal l-Valine hydrochloride. Spectrochimica Acta Part A. 2008; 69: 1283-1286.
4. Mohd Anis, Shirsat MD, Hussaini SS, Joshi B, Muley GG. Effect of sodium metasilicate on structural, optical, dielectric and mechanical properties of ADP crystal. J. Mater. Sci. Technol., 2016; 32(1): 62-67.

5. Anis M, Muley GG, Shirsat MD, Hussaini SS. Comparative characterization study of pure and glycine doped potassium thiourea chloride crystals. Mater. Res. Innovat. 2015; 19: 338-344.
6. Selvaraju K, Valluvan R, Kumararaman S. Growth and characterization of a new metal-organic crystal: Potassium thiourea iodide. Mater. Lett. 2006; 60: 3130- 3132.
7. Madhavan J, Aruna S, Thomas PC, et al. Growth and characterization of l-histidin hydrochloride monohydrate single crystals. Cryst. Res. Technol., 2007; 42: 59-64.
8. Narayan Bhat M, Dharmaprakash SM. New nonlinear optical material: glycine sodium nitrate. J. Crystal Growth, 2002; 235: 511-516.
9. Azhar SM, Mohd Anis, Hussaini SS, Kalainathan S, Shirsat MD, Rabbani G. Doping effect of l-cystine on structural, UV?visible, SHG efficiency, third order nonlinear optical, laser damage threshold and surface properties of cadmium thiourea acetate single crystal. Optics & Laser Technology, 2017; 87: 11-16.
10. Mohd Anis, Hussaini SS, Shirsat MD. A systematic study on electrical and physical properties of calcium bis-thiourea chloride crystal. Optik, 2016; 127: 9734-9737.
11. Subashini A, Rajarajan K, Suresh Sagadevan. Synthesis, growth, spectral, optical and thermal studies of thiourea family crystal, Mater. Res. Express. 2017;4: 026202-204.
12. Linga Raju Ch, Narasimhulu KV, Gopal NO, Rao JL, Reddy BCV. Spectral studies on VO^{2+} ions in potassium thiourea bromide single crystals using EPR and optical absorption spectroscopy. J. Molecular Structure. 2005: 754: 100–105.
13. Sudhakar Reddy B, Gopal NO, Narasimhulu KV, Linga Raju Ch, Rao JL, Reddy BCV. EPR and optical absorption spectral studies on Mn2+ ions doped in potassium thiourea bromide single crystals. J. Molecular Structure. 2005;751:161– 167.
14. Krishnan C, Selvarajan P, Freeda TH. Growth and studies of pure and potassium iodide-doped zinc tris-thiourea sulphate (ZTS) single crystals. J. Crystal Growth. 2008; 311:141-146.
15. Goma S, Padma CM, Mahadevan CK, Dielectric parameters of KDP single crystals added with urea. Materials Letters, 2006; 60: 3701-3705.
16. Shanthi A, Krishnan C, Selvarajan P, Growth and characterization of a single crystal of Urea Adipic acid (UAA) – A third order nonlinear optical material. Spectrochimica Acta Part A, 2014;122:521–528.
17. Selvaraju S, Valluvan R, Kumararaman S. A new metal-organic crystal: Potassium thiourea chloride. Mater. Lett. 2007; 61:751-753.

18. Watanbe I, Okumura ., Annealing Behavior of Amorphous C:H Films Prepared by Glow Discharge Decomposition of CH_4 and H_2. Jpn. J. Appl. Phys. 1986; 25:1851-55.
19. Eya DDO, Ekpunobi AJ and Okeke CE. Influence of thermal annealing on optical properties of tin oxide thin films. Acad. Open Internet J. 2006; 17: 1311-1320.
20. Abu El-Fadl A. Electrical properties of K_2ZnC_{l4} crystals pure and doped with CO_2+ ions between 300 and 500 K. Eur. Phys. J. AP. 6 (1999) 257-262.
21. Kurtz SK, Perry TT. A powder technique for the evaluation of nonlinear optical materials, J. Appl. Phys. 1968; 39: 3798-3813.
22. Fischer-Cripps AC. Elastic-plastic response of materials loaded with a spherical indenter. J. Mater. Sci. 1997; 32: 727-736.
23. Sangwal K. On the reverse indentation size effect and microhardness measurement of solids. Mater. Chem. Phys. 2000; 63: 145-152.
24. B. Wolf B. Inference of mechanical properties from instrumented depth sensing at tiny loads. Cryst. Res. Technol. 2000; 35: 377-399.
25. E. Meyer, Contribution to the Knowledge of Hardness and Hardness Testing. Z. Ver, Dtsch. Ing. 1908; 52: 645-654.
26. Onitsch EM. Über die Mikrohärte der Metalle. Mikroscopia. 1947; 2: 131-151.
27. Suresh S, Ramanand A, Jayaraman D. Mechanical properties of L-Valine Single crystals, Optoelectronics and Advanced Materials-Rapid Communications. 2010; 4(12): 1987-1989.
28. Wooster WA. Physical Properties and Atomic Arrangements in Crystals, Rep. Prog.Phys.16 (1953) 62-82.
29. Selvarajan P, Das BN, Gon HB, Rao KV. Dielectric properties of quenched and laser-excited or field-treated LiF single crystals irradiated with X-rays. J.Mat.Sci. 1994; 29: 4061-4064.
30. Rao KV, Samakula A. Dielectric properties of cobalt oxide, nickel oxide and their mixed crystals.J.Appl.Phys. 1965; 36: 2031-2038.
31. Prasad NV, Prasad G, Bhimasankaran T, Suryanarayana SV, Kumar GS. Studies in $(NH_4)_{(2x)}Cd_{(1-X)}C_2\ O_4$. $3H_2\ O$ crystals grown by gel technique. Indian J. Pure Appl. Phys. 1996; 34: 834-836.