ISSN: 0974-5823 Vol. 7 No. 5 May, 2022

International Journal of Mechanical Engineering

STRUCTURAL, OPTICAL AND MICROHARDNESS CHARACTERISATIONS OF THIOUREA - VANADYL SULFATE COMPOSITE SINGLE CRYSTALS

S.Amirsha Evangelin Kezia

Register No: 21111272132008, Research Centre: St. John's College, Palayamkottai, Tirunelveli District., Tamil Nadu, India (Affiliated to Manonmaniam Sundaranar University, Tirunelveli)

N.Balasundari*

Department of Physics, Sri K.G.S. Arts College, Srivaikuntam-628619, Thoothukudi District, Tamil Nadu, India (Affiliated to Manonmaniam Sundaranar University, Tirunelveli)

N.Vijayakumar

Department of Physics, Sri K.G.S. Arts College, Srivaikuntam-628619, Thoothukudi District, Tamil Nadu, India

(Affiliated to Manonmaniam Sundaranar University, Tirunelveli)

A.Arulgnanam

Department of Physics, St. John's College, Palayamkottai, Tirunelveli District., Tamil Nadu, India

(Affiliated to Manonmaniam Sundaranar University, Tirunelveli)

ABSTARCT: Single crystals of thiourea-vanadyl sulfate (TVS) composite, a new nonlinear optical (NLO) material, were grown from aqueous solution by slow evaporation technique at room temperature. The solubility was carried out at various temperatures. The salt has positive temperature coefficient of solubility. The crystal system and unit cell parameters of the grown crystals were confirmed by X-ray diffraction (XRD) analysis. FTIR spectrum provides the information about the presence of functional groups. A band gap of 3.78 eV is ascertained from UV−Vis−NIR spectroscopy. The mechanical properties of the grown crystals were evaluated by Vickers micro-hardness test and the result reveals the soft nature of the grown crystal.

Keywords: Thiourea-Vanadyl Sulfate composite single crystal, Solubility, XRD, FTIR, UV, Hardness

INTRODUCTION

Non-linear optic (NLO) materials have been in demand over the last few decades due to their technological importance. NLO materials capable of generating the second harmonic frequency play an important role in the domain of optoelectronics, photonics laser technology, optical communication, signal processing and instrumentation [1-3]. Thiourea (SC $(NH_2)_2$) is an interesting inorganic matrix modifier due to its large dipole moment and ability to form an extensive network of hydrogen bonds. It belongs to the orthorhombic crystal system [4-7]. NLO materials showing second harmonic generation (SHG) have been in demand over the last several decades due to technological importance [8]. The materials explored for NLO applications were mostly inorganic until the last decade. However, the fact is that inorganic materials have lower probability for centric structures and consequently researchers focused their attention on organic materials. Organic NLO materials are being investigated due to their potentially high nonlinearities and rapid response in electro-optic effect compared to inorganic NLO materials [10]. Due to the above reason, a lot of research has been carried out on semiorganic materials which have combined properties of both organic and inorganic materials [11].

New metal complexes of thiourea and thiourea analogs have been investigated for technological applications [12]. Metal complexes of thiourea, commonly called semi organics, include the advantages of both organic and inorganic part of the complex. Thiourea crystal is the molecular ferroelectric crystal and it has been the subject of many investigations dealing with its physical properties. Thiourea molecules have large dipole moment and have the ability to form extensive network of hydrogen bonds and compounds. Inclusion of thiourea and its derivatives possess specific characteristic of nonlinearity and chemical flexibility forming variety of structures [13]. Based on the importance of thiourea compounds as they mimic the crystalline organic host nature, and vanadyl sulphate ($VOSO_4$) as a typical organic compound, it isvery interesting to study the behavior of this composite material in its single crystal form.

The metallic element vanadium has interesting physical and chemical properties. Among the transition metal ions like VO^{2+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, etc., vanadyl (VO^{2+}) is the most stable diatomic ion which is present in molecular state. Vanadium survives in

several arrangements, including vanadyl sulfate and vanadate. Vanadium fits into the first transition sequence (iron group with unfilled 3dshell) and has electronic configuration $[Ar]^{18}3d^3\ 4s^2$ with electronic spin ½. Vanadyl sulfate is generally found in nutritional supplements. Vanadium as a dopant plays a significant role in refining the optical quality of the doped crystals. The existence of vanadium enriches the optical properties of the VO^{2+} and thus considered as a potential candidate for the fabrication of optoelectronic device applications [14]. Impacted by the above examinations the present work investigates growth, structural and optical characterization of thiourea-vanadyl sulphate (TVS) single crystals.

MATERIALS AND METHODS

Analytical reagent grades (AR) of Thiourea and Vanadyl Sulfate in molar ratio 1:1 were used for the synthesis of thiourea-vanadium sulfate (TVS) composite. The calculated amounts of Thiourea-Vanadyl sulfate were dissolved in double distilled water (DDW). The mixture was stirred vigorously at room temperature for 3h. The solution was filtered using wattman filter paper to prevent nucleation of any insoluble impurities present in the solution. The filtered solution was covered with a porous cover. Optically transparent crystals of TVS were grown in the period of 20 days by slow evaporation technique. Photograph of the grown crystals is shown in Figure. 1

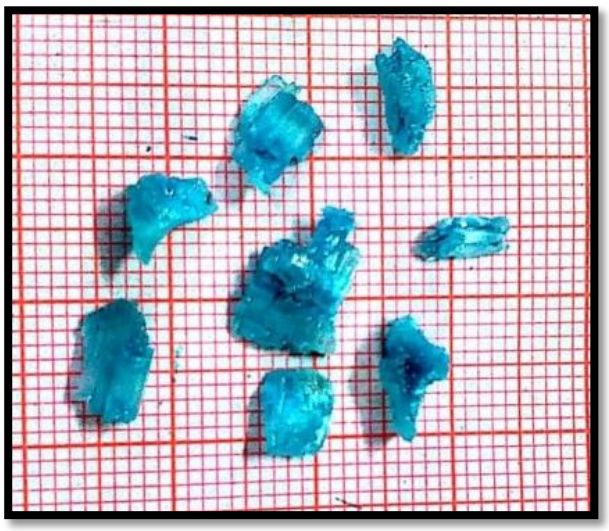

Figure 1. Photograph of TVS crystals

SOLUBILITY

The solubility of the synthesized crystal was carried out using a hot-plate magnetic stirrer and a digital thermometer. In solution method, the crystal size depends on the amount of solute available in the solution and it is decided by the measurement of solubility. Solubility of a material in a particular solvent defines the super-saturation which is the driving force for the rate of crystal growth. Hence solubility studies are essential for solution method of crystal growth. Initially the temperature of the hot plate was maintained at room temperature i.e. 30 °C. 50 ml of DDW was kept in an air tight glass container and placed on the hot-plate of the magnetic stirrer. The synthesized salt was added slowly with it and stirred until a small precipitate was formed. This confirmed the supersaturated condition of the solution. Then 25 ml of the solution was pipetted out and taken in a petri dish. It was heated up at 45 °C till the solvent was evaporated. The weight of the salt was measured and the solubility (g/100 ml) of the synthesized salt was determined gravimetrically [15,16]. The same procedure was adopted to determine the solubility of the salt at various temperatures. The study of variation of solubility of the synthesized salt with temperature is shown in Figure 2. It was observed from the Figure 2 that the solubility of the salt increases with the increase of temperature. Since the solubility increases with temperature, the salt has positive temperature coefficient of solubility. The increase in solubility may lead to the change in thermodynamic parameters viz. surface concentration of growth species, the surface energy, change in growth rate and change in morphology. Saturated solutions were prepared using the solubility data and the seed crystals were obtained in a period of 20 days using slow evaporation technique. Bulk crystals of TVS were grown from the saturated solutions using slow evaporation technique [17].

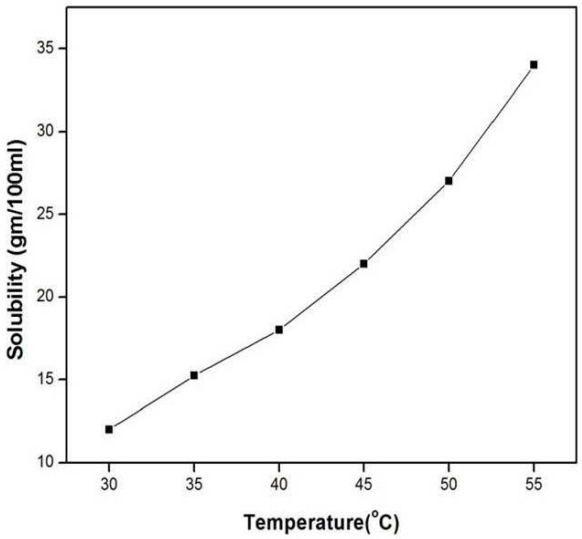

Figure 2. Variation of solubility with temperature

CHARACTERIZATION TECHNIQUES

The powder X-ray diffraction (XRD) was performed on a using P - Analytical X'Pert Pro Philips X-diffractometer. The samples were examined with Cu Kα (λ=1.5406Å) radiation. Single crystal XRD was carried out using Enraf Nonius CAD4 diffractometer with Mo Kα (λ =0.7170 Å) The FT-IR spectra were recorded on SHIMADZU – IR AFFINITY – 1S Model spectrophotometer by KBr pellet technique in the range 4000–400 cm^{-1}. The UV–visible transmittance spectrum was recorded on a SHIMADZU Spectrometer UV -1800 in the range 200 nm – 1100 nm. Micro hardness study of the grown crystals was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Indentations were made for various loads. Several trials of indentation were carried out on the prominent face and the average diagonal lengths were measured for an indentation time of 10 sec.

RESULTS AND DISCUSSION

XRD ANALYSIS

The wide angle powder XRD pattern of TVS crystal is shown in Figure.3. The peak angles, d-space values and the corresponding hkl values are presented in Table 1. The sharp peaks indicate the crystalline nature of the grown TVS crystals. The reflections of powder XRD pattern of TVS crystal were indexed using TREOR software adopting the Lipson and Steeple procedure [18]. Single crystal XRD data is presented in Table 2. From the data it is observed that the grown crystals crystallized in triclinic system. Intensity variations are observed because of lattice strain. Major peak (020) of thiourea [19] with maximum intensity is observed in TVS crystal confirms the incorporation of thiourea in crystal. For Thiourea salt, the XRD peaks were reported at about 2θ = 19.80°, 20.68°, 23.20°, 28.30°, 31.24°, 35.30°, 36.18°, 47.04° and 51.59° [JCPDS-09-790]. The XRD pattern of TVS shows a shift in the peak position compared with that of thiourea indicating the inclusion of thiourea and its interaction with vanadyl sulfate.

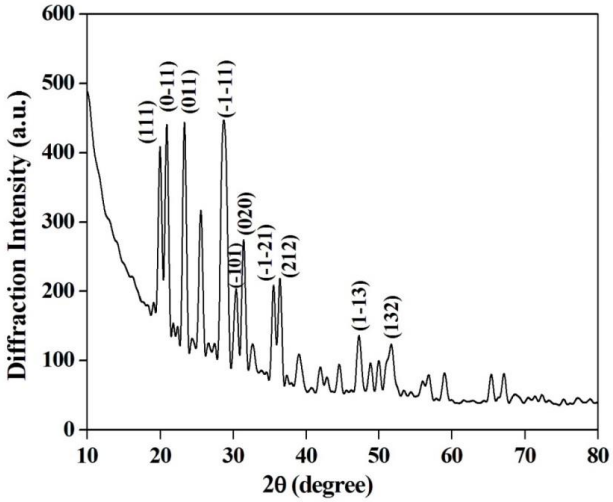

Figure 3. Powder XRD pattern of TVS crystal

Table 1. Powder XRD data of TVS crystal

S. No.	2 θ (degree)	d – spacing	hkl	$\frac{I}{I_{max}}$ %
1	20.0215	4.43494	111	78.03
2	20.8919	4.25210	0-11	100.00
3	23.3093	3.81629	011	95.92
4	28.5139	3.13044	-1-11	89.23
5	29.0124	3.07778	-101	79.84
6	31.4446	2.84505	020	40.88
7	35.5709	2.52391	-1-21	37.42
8	36.3930	2.46876	212	42.16
9	47.1782	1.92650	1-13	15.98
10	51.6705	1.76908	132	14.23

Table 2. Single crystal XRD data of TVS crystal

Sample	Cell Parameters	Volume
Thiourea-Vanadium Sulfate (TVS) Crystal	a = 5.56 (3) Å b = 6.30 (2) Å c = 6.38 (2) Å α = 84.8 (4)° β = 66.0 (5)° γ = 66.3 (7)°	186 (2) $Å^3$

FTIR SPECTROSCOPY STUDIES

Infrared absorption studies are important in the investigation of molecular structure of crystals. This study involves the examination of stretching, bending twisting and vibrational modes of atoms present in a molecule and hence to identify the functional groups of the grown crystals. Figure 4 represents the FTIR spectra of TVS crystal. The assignments for the absorption peaks are given in Table 3. In the region of vanadyl group modes, we observed the peak at 996 cm^{-1} corresponds to V=O stretching mode of vibration. This peak confirms the presence of vanadyl sulfate in the grown crystals [20, 21]. The C=S stretching and C−N stretching vibrations of thiourea appear at 735 cm^{-1} and 1490 cm^{-1} respectively undergo a considerable bathochromic shift to 696 cm^{-1} observed at 1449 cm^{-1} respectively. Hypsochromic shifts are observed in the N−H bending (1600−1614 cm^{-1}). The peaks appear between 2357 and 2566 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of NH_2 group of thiourea. Shifts to lower wavenumbers are also observed for the N−H stretching frequencies in the TVS from 3180 to 3132 cm^{-1} and 3210 to 3189 cm^{-1}. These observations confirmed the strong interaction between thiourea and vanadyl sulfate. Moreover, the N-C-N stretching vibration of thiourea observed at 1093 cm^{-1} appears red-shifted to 1050 cm^{-1} with weak intensity also demonstrating the incorporation of thiourea in the vanadyl sulphate [22]. Obviously, these changes clearly reveal the structural and chemical modifications of TVS crystal.

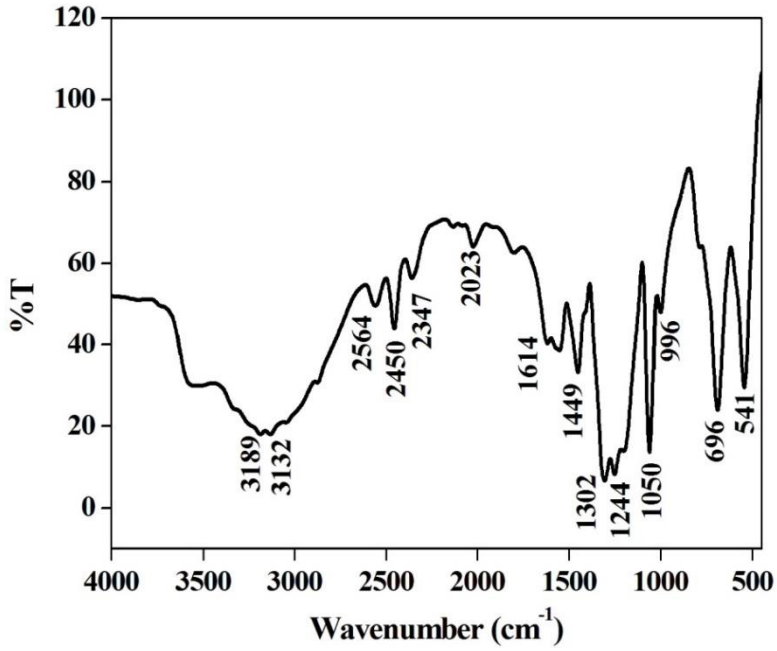

Figure 4. The FTIR spectra of TVS crystal

Table 3. FTIR Spectral assignments for TVS crystal

Wavenumber (cm^{-1})		Peak Assignments
Thiourea	**TVS**	
3280	3189	Asymmetric NH stretching
3180	3132	Symmetric NH stretching
2358	2347	Symmetric stretching modes of NH_2
1600	1614	NH bending
1470	1449	Coupled CN stretching vibration
1063	1050	N-C-N stretching
735	696	C=S bond vibration
492	541	N=C=N rocking mode

UV-VISIBLE-NIR SPECTRAL STUDIES

The single crystals are mainly used for optical applications. Thus the study of optical transmittance of grown crystal is important. Figure 5 shows the transmittance spectrum of TVS crystal. From Figure 4, it is noted that the grown crystal has lower cut-off wave length around 328 nm near UV region, absorption arises from electronic transition associated within the thiourea unit of TVS crystals. The optical band gap was calculated using the formula [23].

$$E_g = \frac{hc}{\lambda} \text{ eV}$$

The band gap of TVS crystal is 3.78 eV. Thus TVS crystals have good transmission in UV as well as in visible region. The wide range of transparency of TVS crystals is an added advantage in the field of optoelectronic applications [24].

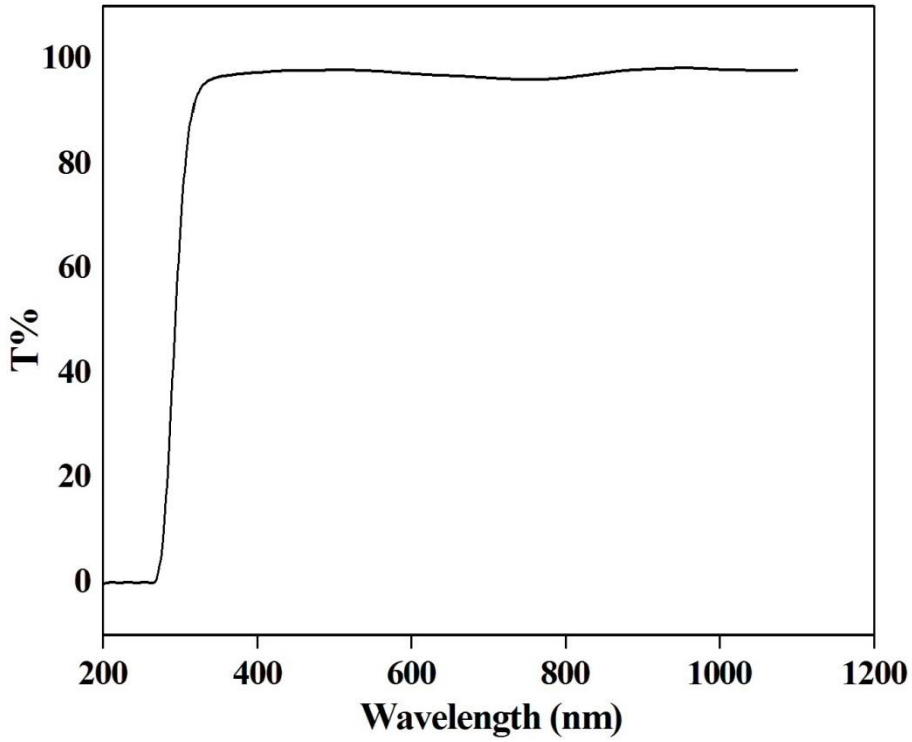

Figure 5.UV-Vis-NIR spectrum of TVS crystal

MEASUREMENT OF HARDNESS

Hardness is as measure of materials resistance to localized plastic deformation. The micro hardness plays a vital role in device fabrication. The hardness of a material is influenced by various parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. Micro-hardness measurement is a general microprobe technique for assessing the bond strength. The chosen smooth surfaces of the crystal were used for the measurement of micro hardness using a Vickers micro hardness tester fitted with a diamond indenter. In micro-hardness testing, an indentation is made on the specimen by a diamond indenter by applying a load P (Figure 6). The size d of the resultant indentation is measured with the help of a calibrated optical microscope. The hardness is evaluated as the mean stress applied below the indenter. Initially the measurement of hardness was used for small components (watch gears, thin wire and foils) and the testing was extended to research studies of individual phases, orientation effects in single crystals, diffusion gradients, ageing phenomena, etc. in metallic and ceramic materials. Now-a-days, testing at temperatures up to 1000 °C is possible. Microhardness tests need to be very carefully controlled and replicated, using as large a load as possible. The indenter is lowered slowly at a rate of <1 mm/min under vibration-free conditions. This condition is achieved within 15 sec, a test period commonly used.

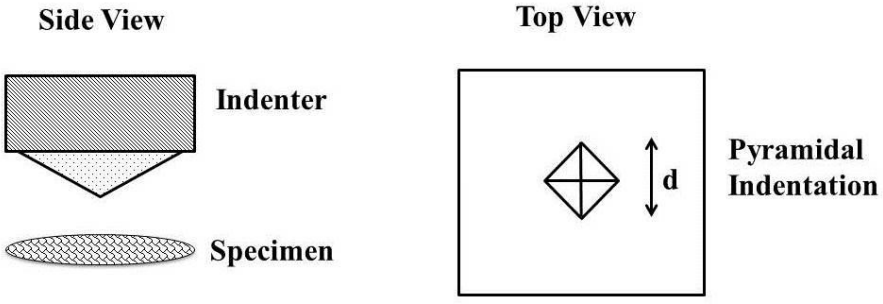

Figure 6. Schematic diagram of indentation.

The Vickers hardness (H_V) of the crystal is calculated using the relation

$$H_v = 1.8544 \ P/d^2 \ \ Kg/mm^2$$

Where P is the applied load in g and d is the length of indentation impression in mm and 1.8544 is a constant of a geometrical factor for the diamond pyramid. The variation of micro hardness number with load for TVS crystal is shown in Figure 7. The hardness increases to a load of 30 g and thereafter decreases for higher loads. It indicates that the hardness is independent with

load for higher values [25-27]. At small loads, the indenter penetrates only to the surface layers and hence the hardness number increases with a small load. The increases of penetration depth with applied load and the overall effect is due to the surface and inner layers. This combined effect is responsible for the nonlinear portion of the curve [28].

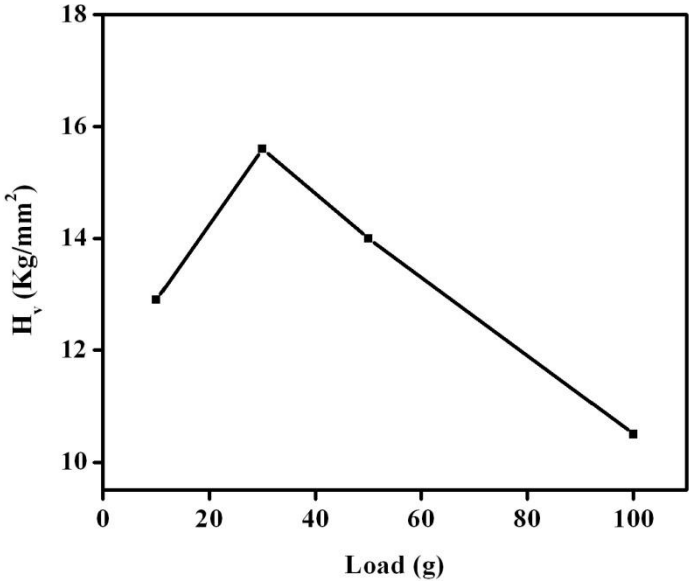

Figure 7. Variation of micro-hardness number with load for TVS crystal

CONCLUSIONS

Optically good quality single crystals of TVS composite were grown by slow evaporation technique at room temperature. Solubility of the sample in water increases with increase of temperature. Since the solubility increases with temperature, the TVS crystals have positive temperature coefficient of solubility. Structure and optical properties of TVS composite have been examined using different techniques such as, XRD, FTIR, and UV-Vis spectroscopy. Single crystal XRD confirms that the grown crystalsbelong to triclinic system. The crystallinity of the grown crystals was confirmed by powder XRD studies. Powder XRD of TVS crystals has been used to index the planes. The results clearly show the overlapping of planes of TVS crystal. The micro-hardness study revealed that the grown crystals are mechanically soft. The presence of thiourea and vanadyl sulfate was confirmed by FTIR analysis. From UV-visible transmittance spectra it is noticed that TVS crystals are quite transparent in the wavelength region from 220 nm to 1100 nm and a cut off wavelength is noticed at 328 nm. Thus, the grown crystal could be a useful candidate for optoelectronic applications in visible and infrared region.

References

1. G. Madhurambal G, M. Mariappan, S.C. Mojumdar, *"Thermal, UV and FTIR Spectral Studies of Urea-Thiourea Zinc Chloride Single Crystal"*.Journal of Thermal Analysis and Calorimetry, Vol. 100, 2010, 763–768.
2. G. Madhurambal, M. Mariappan, S.C. Mojumdar, *"TG-DTA, UVand FTIR Spectroscopic Studies of Urea-Thiourea Mixed Crystal"*, Journal of Thermal Analysis Calorimetry,100, 2010,853–856.
3. S.S. Gupte, C.F. Desai,*"Vickers Hardness Anisotropy and Slip Systeminzinc(tris)thiourea sulfate crystals"*. Crystal Research Technology, 34,1999,1329–1332.
4. S.A.Begum, M.Hossain, J.Podder,*"An Investigation On The Growth And CharacterizationOf Thiourea Single Crystal Grown From Aqueous Solutions"*, Journal Of Bangladesh Academy Of Sciences, Vol. 33, 2009, 63-70.
5. S. Meenakshisundaram, S. Parthiban, N. Sarathi, R. Kalavathy, G. Bhagavannarayana, *"Effects of organic dopants on ZTS single crystal"*, Journal of Crystal Growth, Vol. 293, 2006, 376-381.
6. T.Prasanyaa, M.Haris, V.Mathivanan, M.Senthilkumar, T.Mahalingam, V.Jayaramakrishnan, *"Synthesis and characterization of pure, urea and thiourea doped organic NLO l-arginine trifluoroacetate single crystals"*, Materials Chemistry and Physics, Vol. 147, 2014, 433-438.
7. M. Divya, P. Malliga, P. Sagayaraj& A. Joseph Arul Pragasam, *"Optical Based Electrical Properties of Thiourea Borate NLO Crystal for Electro-Optic Q Switches"*, Journal of Electronic Materials,Vol. 48, 2019,5632–5639.
8. S.Chattopathyay, Y.F. Huang, K-H. Chen and L-C. Chen, *"4-Biomimetic Nanostructures for Anti-Reflection (AR) Devices",* Optical Biometics Materials and Applications, 2012, 108-146.
9. S.Vasumathi, H.JohnsonJeyakumar, P.Selvarajan, *"Growth, spectral, NLO, hardness, Hirshfeld and antibacterial activity studies of melaminiumcyanoacetate monohydrate crystals"*, Journal of Molecular Structure, Vol.1263, 2022,

10. SU.Narmatha, S.R.Thilagavathy, *"Effect of thiourea on the growth, optical, thermal, mechanical and dielectric properties of potassium hydrogen phthalate crystal"*, Materials Today: Proceedings ,Vol. 48, 2022, 394-399.

11. P.A. Franken, A.E. Hill, C.W. Peters, G.Weinreich. *"Generation of Optical Harmonics"*, Physical Review Letters, Vol. 7, 1961, 118-120.

12. M. Mariappan, G. Madhurambal, B. Ravindran, S. C. Mojumdar, *"Thermal, FTIR and microhardness studies of bisthiourea-urea single crystal"*, Journal of Thermal Analysis Calorimetry,Vol.104, 2011,915-921.

13. K.D.M. Harris,"*Meldola Lecture: understanding the properties of urea and thiourea inclusion compounds"*, Chemical Society Reviews, 26, 1997, 279-289.

14. K. Juliet sheela, S. Nandhini, *"Structural, optical, dielectric and EPR properties of vanadium-doped lithium sulfate monohydrate single crystal for optoelectronic applications"*, Journal of Materials Science: Materials in Electronics", Vol. 32, 2021, 16916-16926.

15. A.S.J. Lucia Rose, P. Selvarajan, S. Perumal, *"Growth, structural, spectral, mechanical, thermal and dielectric characterization of phosphoric acid admixtured L-alanine (PLA) single crystals"*, SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy, Vol. 81, 2011, 270-275.

16. N. TheresitaShanthi, P. Selvarajan, C.K. Mahadevan,*"Growth, structural, mechanical, spectral and dielectric characterization of NaCl-added Triglycinesulfate single crystals"*, Current Applied Physics, Vol. 9, 2009, 1155-1159.

17. N. Balasundari, P. Selvarajan, S. Lincy Mary Ponmani, D. Jencylin, *"Studies on Growth and characterization of urea-doped diglycine picrate (DGP) single crystals "*, Recent Research in Scienceand Technology, Vol. 3, 2011, 64-67.

18. H. Lipson, H. Sleeple, *"Interpretation of X-ray powder Diffraction Patterns*", Fifth edition, Mcmillan, Newyork, 1970.

19. T. Fahmy, A. Sarhan, Z.M. Elqahtani, *"International Journal of Engineering Research and Technology"*, Vol. 13, 2020, 454-461.

20.C. O'Dwyer,a,z V. Lavayen,a,b S. B. Newcomb,c M. A. Santa Ana,b E. Benavente,d

G. González,b and C. M. Sotomayor Torresa,*"Vanadate Conformation Variations in Vanadium Pentoxide Nanostructures"*, Journal of The Electrochemical Society, 154**,** 2007**,** 29-35.

21. http://wwwchem.uwimona.edu.jm/courses/vanadium.html

22. DevendraTiwari, David J. Fermin, T. K. Chaudhuri,Arabinda Ray, *"Solution Processed Bismuth Ferrite Thin Films for All-Oxide SolarPhotovoltaics"*, The Journal of Physical Chemistry - C, Vol. 119,2015, 5872-5877.

23.D. Jencylin, P. Selvarajan, S. Lincy Mary Ponmani and N. Balasundari, "*Studies on growth and characterization of glycine lithium sulphate (gls) doped with l-arginine*", International Journal of Current Research Vol. 4, 2012, 119-122.

24.G. Rajaduraia, A. Puhal Raja and S. Pari "*Synthesis, Growth, Structural, Spectroscopic, Thermal and Optical Properties of Semiorganic Material-Tristhiourea Cadmium Sulphate (TTCS)"*,Scholars Research Library, Archives of Physics Research, 4(3), 2013, 61-66.

25. P.N. Kotru, A.K. Razdan, B.M. Walkyn,*"Microhardness of flux grown pure doped and mixed rare earth aluminates and orthochromites"*, Journal of Materials Science, 24, 1989, 793-803.

26. C.Desai, J.L. Raj, *"Microhardness studies of SnI_2 and SnI_4 single crystals"*, Bulletin of Materials Science, 5, 1983, 453-457.

27. K. Sangwal, *"On the reverse indentation size effect and microhardness measurement of solids"*Materials Chemistry and Physics, 63, 2000, 145-152

28. C. Besky Job, J. Benet Charles, *"Growth, structural and micro-hardness studies of KSb_2F_7 and KSb_4F_{13} crystals",* Indian Journal of Pure & Applied Physics, Vol. 49, 2011, 820-824 .