Growth and Characterization of Potassium (Tris) Thiourea Sulphate Single Crystals

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Abstract: The Potassium Tris (thiourea) sulphate single crystals were grown using slow evaporation method. The unit cell parameters of the grown crystal are determined with the help of single XRD analysis. The various functional groups of the grown PTS crystal are determined with the help of FTIR analysis. The optical properties of PTS single crystal are determined by UV-Vis spectral studies. The Florescence spectrum of PTS crystal shows the strong emission in the visible region at 569.94 nm. The hardness of the material is also measured by Vicker's Hardness Tester.

Keywords - **Crystal growth, Single XRD, UV-Visible Spectroscopy, Fluorescence analysis etc.**

I. INTRODUCTION

In recent years, the utility of crystals has been reached out from ornaments to a few helpful applications in optics, electronics and electrical devices. Advance in precious crystal development is exceedingly requested in the perspective of its recent advancements in the fields of semiconductors, nonlinear optic, piezoelectric, photosensitive materials and crystalline thin films for microelectronics and computer industries. The single crystals play a vital role in modern technology. The constituents of the crystals and their inner parts were investigated, analyzed and comprehended with the help of modern spectroscopic techniques. The external shape and planes were correlated with the internal atomic content and their arrangements in unequivocal terms, leads to grow a science named as the investigation of "crystal growth and characterization".

Among many techniques, the slow evaporation technique is the simplest method to grow single crystals. The growth of bis (thiourea) cadmium chloride (BTCC) single crystals and growth and characterization of zinc thiourea chloride (ZTC) have already been investigated [1-2]. Pure thiourea single crystals have been grown from aqueous solution by slow cooling technique are also analyzed [3]. The single crystal of thiourea potassium iodide was successfully grown by the slow evaporation method at room temperature and its dielectric and also NLO properties are studied [4]. Tris thiourea added potassium chloride single crystals, Single crystals of pure and urea doped potassium sulphate and thiourea added potassium and magnesium sulphate were grown by the slow evaporation method and their properties are investigated [5 -7]. Tris thiourea added magnesium sulphate and Tris thiourea added Zinc sulphate have already been reported [8 & 9].

In perspective of finding good quality single crystals, in the present investigation, an endeavor has been made to grow potassium sulphate added tris thiourea single crystals by slow evaporation of the solvent technique and their properties such as single X- Ray diffraction studies (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Visible-NIR, Photoluminescence and mechanical strength are analysed. Hereafter, we name the potassium sulphate added tris thiourea single crystals as PTS crystals.

II. EXPERIMENTAL PROCEDURE:

Crystal growth

The Potassium (tris) thiourea sulphate (PTS) single crystals were grown by dissolving the AR grade potassium sulphate and thiourea in deionized water in the stoichiometric molar proportion 1:3. The compounds well dissolved in deionized water, by stirring them thoroughly using a magnetic stirrer until the solution is well liquefied. Now, the solution is kept undisturbed in a dust free atmosphere in a clean beaker and its top is covered by an aluminum foil sheet with some punched holes. At room temperature, the PTS crystals are grown by slow evaporation technique. PTS single crystals are synthesized by the following reaction,

$$\mathbf{K_2SO_4 + 3CS\,(NH_2)_2 \longrightarrow K_2\,[CS\,(NH_2)_2]_3\,(SO)_4}$$

After 12 – 17 days, good quality PTS single crystals are harvested. The grown crystals are stable and transparent. The figure – 1, is the photograph of grown PTS crystals.

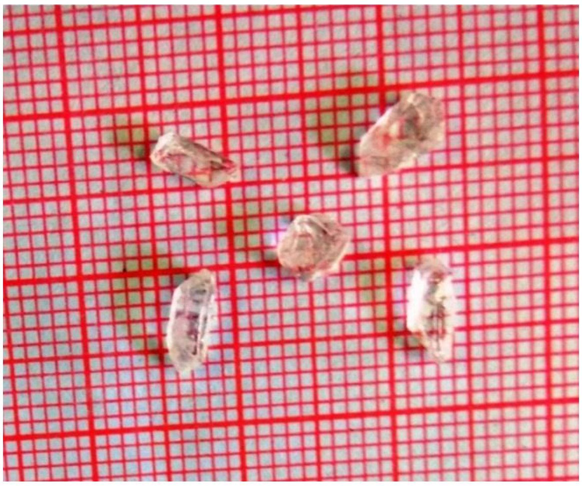

Figure - 1. As grown PTS crystal

III. RESULTS AND DISCUSSION

The grown crystals are undergone to different characterization techniques. The grown crystals of PTS were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The functional groups are identified using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm^{-1}. The optical characteristics of the grown crystals were analyzed in the range of 190 and 1100 nm using LAMBDA-35 UV-Vis-NIR spectrometer. The Vickers hardness measurement was made on the crystal using Shimadzu (Japan) HMV-2 hardness tester. The fluorescence spectrum was recorded by VARIAN Cary Eclipse Fluorescence Spectrophotometer employing 150 Watts Xenon arc discharge lamp as the excitation source.

3.1. Single crystal X-ray diffraction analysis

The single crystal X-ray diffraction is a non-ruinous investigative strategy which yields itemized data about the inner grid of crystalline substances, unit cell measurements and nuclear positions inside the unit cell from a little piece of material. To decide the cross section parameters and volume of the developed PTS single crystals, they were subjected to single crystal X-ray diffraction analysis using Bruker Smart Apex2 single crystal X-ray diffractometer. From the analysis, it is found that the grown crystal is belonging to orthorhombic crystal system with space group Pmcn. The lattice parameters are: a = 5.83 A°, b = 7.53 A° and c = 10.15 A° and the volume of the grown crystal is 446 A°^{3}.

3.2. FTIR Spectral Studies

The FTIR spectrum of the grown PTS single crystals is recorded in the range 400 - 4000 cm^{-1}, using Perkin-Elmer spectrometer and is shown in Figure 2. The frequencies of the PTS single crystals are observed. The peak at 3379 cm^{-1} is assigned to O-H symmetric stretching vibration of water molecule [11,15]. The NH$_2$ symmetric stretching vibration is observed at 3172 cm^{-1}. At 2686 cm^{-1}, the C-H stretching vibrations are occurring for the grown crystals. The C=C stretching vibrations for the grown crystals appear at 1614 cm^{-1}. The prominent peaks at 1592 and 1469 cm^{-1} are due to C-C stretching and C-H bending respectively. The grown crystals exhibits absorption peaks at 1415 cm^{-1} due to C=S asymmetric stretching vibrations. The peak near 1085 cm^{-1} is due to N-C-N stretching. The peak at 730 cm^{-1} is due to C=S symmetric stretching vibrations [9.11]. The peak at 489 cm^{-1} confirms the presence of sulphate ion. The S-C-N asymmetric bending is also observed at 624 cm^{-1}.

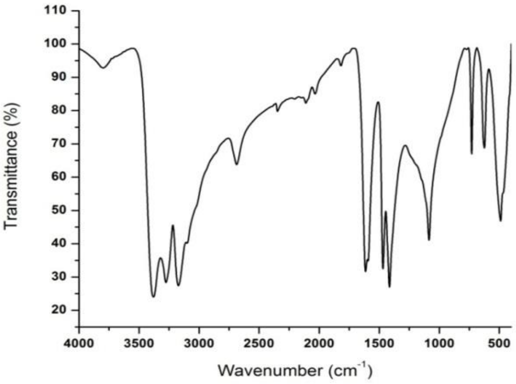

Fig- 2. FTIR Spectrums of PTS

3.3. UV – Visible Spectral Analysis

The investigation of optical transmission of the grown crystal is done by utilizing Perkin Elmer Lambda 35 UV-Visible spectrophotometer in the wavelength limit of 190 to 1100 nm. The grown crystal exhibits lower cutoff wavelength around 235.35 nm while analyzing the absorption spectra [10]. The figures 2(a) and 2(b) show the absorption and transmittance spectra of grown PTS single crystals. The figure 3 shows the Tauc's plot of PTS crystal. From tauc's plot, the energy gap of the PTS single crystal is calculated [9, 10]. The optical band gap energy was found to be 2.2 eV.

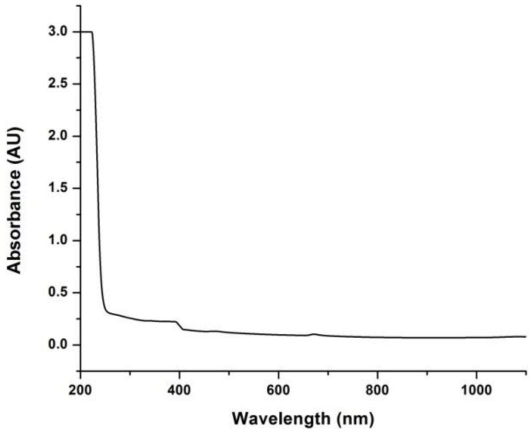

Fig - 2(a). UV-Vis Absorption spectrum of PTS crystal

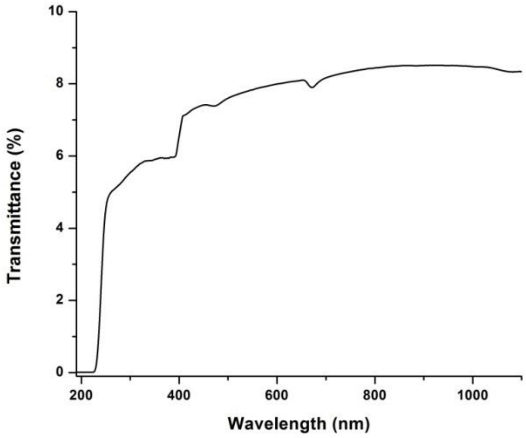

Fig - 2(b). UV-Vis Transmittance spectrum of PTS crystal

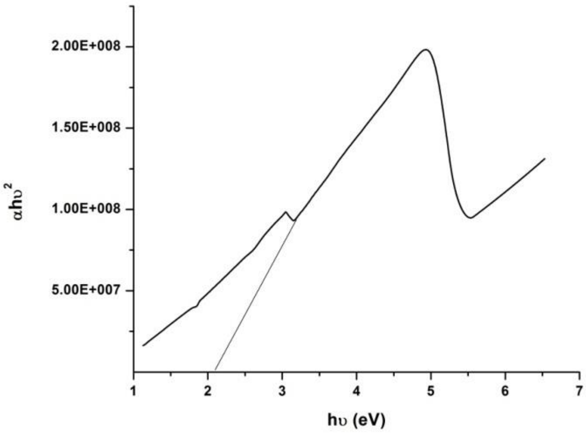

Fig - 3. Tauc's Plot of grown PTS crystal

3.4. Vicker's Hardness Test

The Vicker's hardness test is the more solid technique for estimating the hardness of the substances. Hardness studies is completed on the developed PTS single crystals by a static indentation test at room temperature utilizing a Leitz Wetzlar Vickers micro hardness analyzer fitted with a Vickers diamond pyramidal indenter appended to an occurrence light microscope. A few indentations were made on the crystal by differing the loads from 25 gm to 100 gm and the hardness number (Hv) was found. The indentation time was kept as 15s for every one of the loads. As miniaturized scale splits were produced on the crystal surface at higher burdens, the greatest connected load was constrained to 100 gm [11, 12].

The hardness number was calculated using the relation,

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

where, H_v is the Vickers micro hardness number, P is the applied load in kg and d is the diagonal length of the indentation impression in the millimeter.

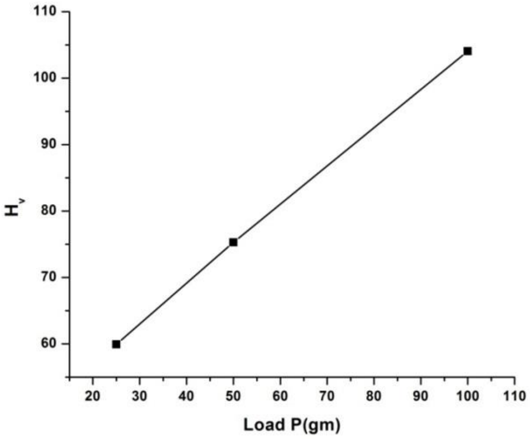

Fig- 4 (a). The Load P Vs Hardness of the grown PTS crystal

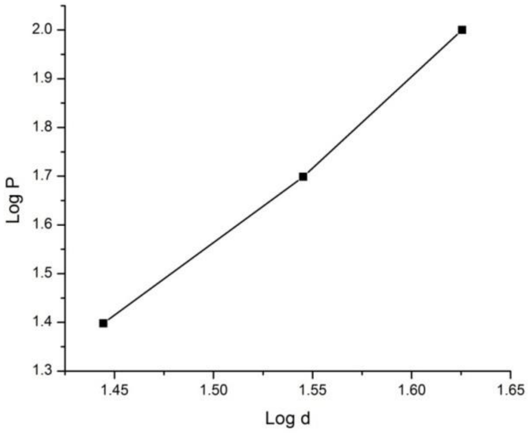

Fig- 4 (b). The Log d Vs Log P of the grown PTS crystal

The Meyer's index number was calculated from the Meyer's law, which relates the load and indentation diagonal length.

$$\log P = \log k + n \log d$$

where, *k* is the material constant and *n* is the Mayer's index or work-hardening coefficient. By plot a graph, log P *vs* log d, for the grown crystals, as shown in Figure 4(b), the value of '*n*' was determined. The slope of the graphs, will give the work hardening index (n) which is found to be 2.981 for PTS [9, 11].

3.5. Fluorescence spectrum

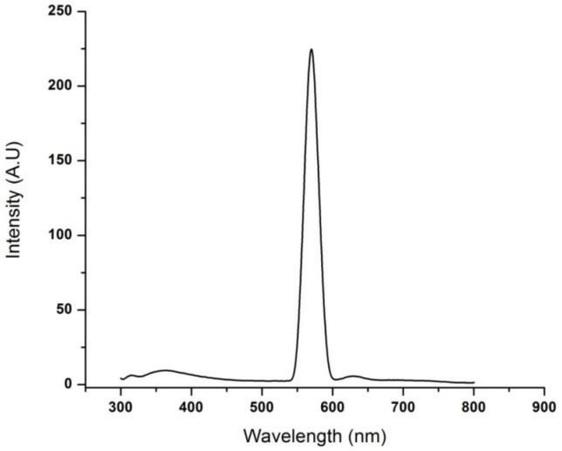

Fig- 5. Fluorescence spectrum of grown PTS crystal

The grown PTS single crystals are subjected to fluorescence studies utilizing fluorescence spectrometer. The spectrum recorded by the emission of photons is an immediate method to measure the band gap energy. The figure 5 shows the emission spectrum of PTS single crystals. The crest at 569.94 nm is observed in the emission spectrum of pure PTS [13]. The band gap energy (E_g) of the grown crystal is calculated by the relation,

$$E = \frac{hc}{\lambda} \text{ Joule}$$

where,

h is the Planck's constant (J.s), c is the velocity of light (m/s) and
λ is the wavelength in nanometer [13, 14].
The band gap energy of the grown PTS crystal is 2.18 eV.

IV. CONCLUSION

The PTS single crystals were grown by slow evaporation technique within three weeks. The orthorhombic system with space group (Pmcn) is affirmed by utilizing the single XRD analysis. The functional groups and vibrational modes have been analyzed by the FTIR spectrum. The lower cut-off wavelength for the PTS single crystal is observed to be 195.85 nm and 235.35 nm respectively, by the UV-Vis absorption spectrum. The grown PTS crystal displays good transmittance property. So it is suitable for optoelectronic device fabrication. From UV absorption study, the band gap energy was found to be 2.2 eV. The mechanical stability of the grown crystal was analyzed by Vicker's micro hardness studies. From the hardness results, it is seen that, the grown PTS single crystals belong to soft material category. The fluorescence spectrum of the grown PTS single crystal exhibits the green emission of 569.94 nm and the band gap energy was 2.18 eV. It confirms that, the material can be used in optoelectronic applications.

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