Growth and characterization of Potassium Thiourea Sulphate

S. SURENTHERABABU*, P. RAJASEKARAN
Department of Physics, Kalaignar Karunanidhi Institute of Technology, Coimbatore-641402, India

Potassium thioureasulphate (PTS) crystals have been synthesized by slow evaporation method using water as a solvent. The spectral bands have been compared with similar thiourea complexes using FTIR spectrum in the range 400 – 4000 cm^{-1}. Optical transmittance of the grown crystal has been studied by using UV-VIS spectrometer. The mechanical strength and work hardening coefficient of the grown crystal have been analyzed by Vicker's microhardness method.

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1. Introduction

In order to satisfy the day-to-day technological requirements, many scientists focused their attention on the growth of materials which have a good nonlinear optical behavior and be optically transparent in the visible and near IR regions. NLO materials play an important role in the field of fiber optic communication, laser technology, optical signal processing in the area of opto-electronics, telecommunication, and optical storage devices [1-6]. Recent works show that the organic crystals have large nonlinear susceptibilities than the inorganic one, but it has low laser damage threshold, inadequate transparency, poor optical quality, lack of robustness, inability to produce large crystals. In the case of inorganic NLO materials, though they have excellent mechanical and thermal properties, they have relatively modest optical linearities due to the lack of extended π – electron delocalization [7, 8]. Hence in last several years research is focused on new types of NLO materials which combine the advantages of organic and inorganic materials called semi-organic materials. Two types of semi-organic materials include organic and inorganic salts and metal organic coordination complexes [9-14]. Due to the high optical nonlinearity and chemical flexibility of organics combined with temporal and thermal stability and excellent transmittance in UV-Visible region [10- 14], the metal organic complexes have great attention in NLO field. The thiourea is an inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [15]. The centrosymmetric thiourea molecule, when combined with inorganic salt yield noncentrosymmetric complexes, which has the nonlinear optical properties [16].

2. Experimental

2.1 Synthesis and crystal growth

By mixing equal ratio of aqueous solutions of Potassium sulphate and thiourea in the stoichiometric ratio 1: 1 the PTS salt has been synthesized. The required quantity of potassium sulphate and thiourea is estimated from the chemical reaction.

$$K_2SO_4+(NH_2CSNH_2)\rightarrow K_2(NH_2CSNH_2)\,SO_4$$

The required weight of salts are salts of very well dissolved in double distilled water and thoroughly stirred to avoid the co-precipitation of the salts by using a magnetic stirrer. Successive recrystallization process has been carried out to improve the purity of the synthesized salt. To avoid decomposition of the solute molecules, the mixer is heated up to 50 ˚C. The PTS crystals are grown from aqueous solution by slow evaporation technique which is non-hygroscopic. Good optically transparent PTS crystal has been crystallized with well defined faces in a period of 25 days which are as shown in Fig.1.

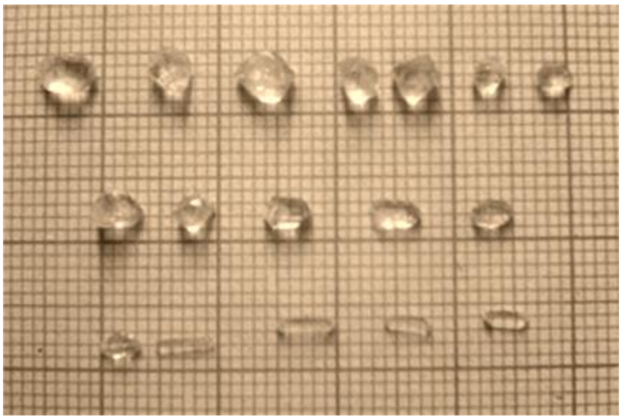

Fig. 1. Photograph of PTS single crystals.

3. Results and discussion

3.1. FT-IR spectral studies

The Fourier Transform Infrared spectroscopy is effectively used to identify the functional groups present in the crystals. The powdered specimen of PTS crystal has been subjected to FTIR analysis by PERKIN ELMER SPECTRUM RXI Fourier Transform Infrared Spectrophotometer using KBr pellet technique in the wavelength range between 400 and 4000 cm^{-1}. The observed bands along with their vibrational assignments have been tabulated as shown in Table 1. The FTIR spectra of thiourea and PTS are shown in the Fig. 2 and Fig. 3 respectively. Crystal structure investigations of thiourea have established the co-planarity structure of C, N and S atoms in the molecule [17]. In the complex, due to the double centers for thiourea, there is a possibility to coordinate with potassium in two ways i.e., through nitrogen or sulfur [18] of thiourea. The high frequency N-H absorption bands in the region 3179– 3395 cm^{-1} in the spectrum of thiourea have not been shifted to lower frequencies on the formation of metal thiourea complex which indicates that the bond is only between sulfur and potassium atoms and not of nitrogen and potassium atoms [19]. The symmetric and asymmetric C=S stretching vibrations at 729 and 1395 cm^{-1} of thiourea are shifted to low frequency region at 617 and 1387 cm^{-1} in PTS respectively which confirms the formation of metal sulphur coordination bond [18]. C=S stretching vibration at 1089 cm^{-1} is shifted to higher frequency 1117 cm^{-1} shows the binding of potassium with thiourea is through sulphur [20]. NH_2 bending at 1621 cm^{-1} is shifted to higher frequency region at 1635 cm^{-1}, asymmetric bending of NH_2 at 3395 cm^{-1} and that of thiourea shifted to higher frequency region at 3441 cm^{-1}.

Table 1. Assignment of IR band frequencies (cm^{-1}) of thiourea and PTS.

Thiourea cm^{-1}	PTS cm^{-1}	Assignment
729	617	C=S stretching
1089	1117	C=S stretching
1395	1387	C=S asymmetric stretching
1621	1635	NH_2 bending

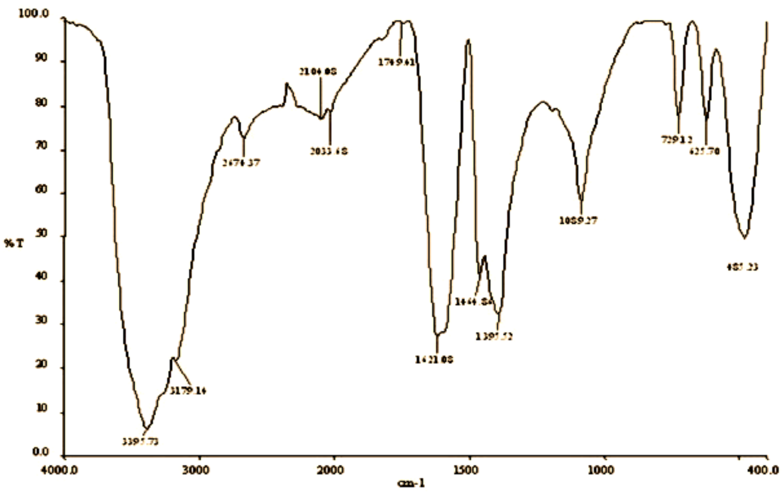

Fig. 2. FTIR Spectrum of thiourea.

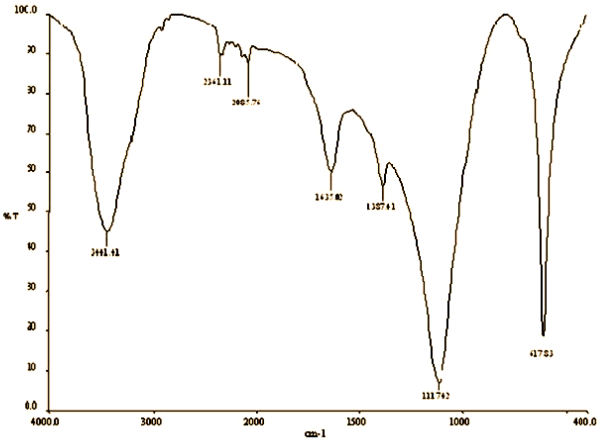

Fig. 3.FTIR Spectrum of PTS.

3.2. Optical studies

Transmission spectra are very important for any NLO material because an NLO material can be used for practical purposes only if it has a wider transparency window. To determine the suitability and transmission range of the PTS single crystal for optical applications, the UV-Visible spectrum has been recorded in the range 190 – 1100 nm by using LAMBDA-35 UV-Vis spectrometer. The recorded spectrum of thiourea and PTS are shown in the Fig. 4 and Fig. 5 and the lower cutoff wavelength of thiourea and PTS are around 220 nm and 232 nm respectively. This π electron dislocation is responsible for its nonlinear optical responses and absorption in near UV region [21]. Thus the grown crystal has got a good transmission in UV as well as in visible region 232 – 1100 nm. The wide range of transparency of grown crystal is an added advantage in the field of optoelectronic application [22].

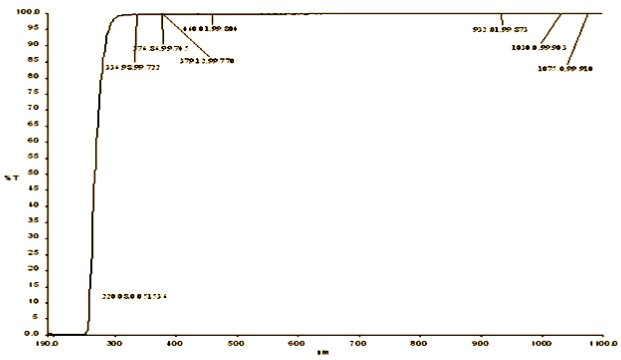

Fig. 4.UV-Vis Spectrum of thiourea.

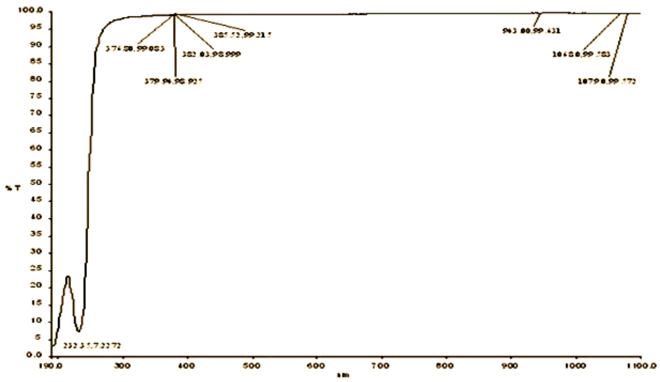

Fig. 5.UV-Vis Spectrum of PTS.

3.3. Mechanical property

Hardness is a measure of the resistance to plastic deformation [23]. This permanent deformation can be achieved by indentation, bending, scratching or cutting. The hardness of the crystal carries information about the strength, molecular bindings, yield strength and elastic constants of the material. The mechanical property of the PTS crystals has been studied using microhardness tester, fitted with a Vickers's diamond pyramidal indenter. A well polished PTS crystal has been placed on the platform of Vickers microhardness tester and the loads of different magnitudes have been applied in a fixed interval of time. Vickers microhardness values have been calculated by using the formula $Hv = 1.8544 \times P/d^2$ Kg/mm^2. Where Hv is the Vickers microhardness number, where P is the applied load (in Kg), d is the mean diagonal length of the indentation impression (in mm) and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. The hardness values have been taken for various applied loads over a fixed interval of time. A graph has been plotted between hardness number (Hv) and applied load (P) as shown in the Fig. 6. The nonlinear behavior of the microhardness of the crystal may be due to cleavage plane of the sample. Hardness value of crystal differs from one plane to another which confirms the microhardness anisotropy.

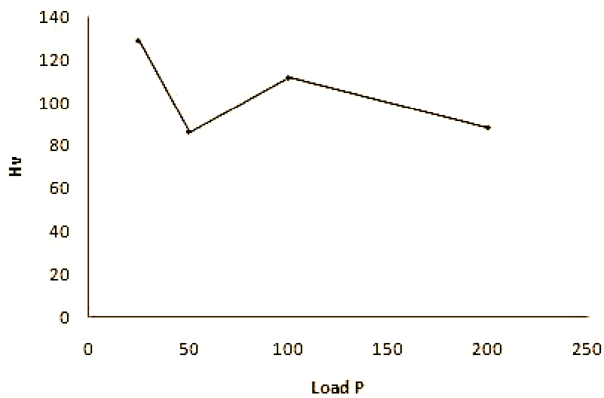

Fig. 6.Variation of Hv with load P.

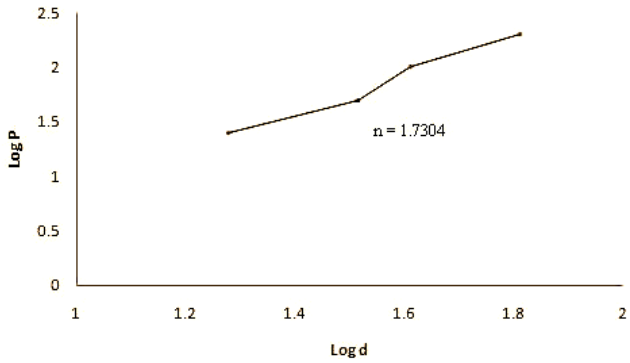

Fig. 7. Log (P) Vs log (d).

At lower loads there is decreases in the hardness with load, which can be attributed to the work hardening of the surface layers. The relation connecting the applied load (P) and diagonal length (d) of the indenter is given by the Meyer Law [24]. $P = ad^n$ where 'n' is the Meyer Index or work hardening coefficient and 'a' is the constant for a given material. A graph has been plotted between log (P) Vs log (d) as shown in the Fig.7.

The slope of the straight line by least squares fit method gives Meyer Index number / work hardening index and it is 1.7304. Hv should increase with the increase of P if n>2 and decrease if n<2. From the observations on various materials Onitschnn [25] and Hanneman [26] pointed out that n' lies between 1 and 1.6 for moderately hard materials.The slope of 1.7304 reveals that the material has moderately hard materials.

4. Conclusion

Single crystals of PTS were successfully synthesized and the crystals were grown by solution growth technique by using water as the solvent. Their optical and mechanical properties are studied. The various functional groups present in PTS are analyzed by FTIR Spectrum. The hardness of the crystal is good and they are suitable for NLO applications. The transparency nature of the crystal in the visible and infrared regions and it has a lower UV cutoff of 232 nm and has a transmittance of 99% are good expected characteristics for NLO materials.

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*Corresponding author: surensoft@yahoo.co.in