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The structural, optical and thermal properties of Tristhiourea potassium chloride crystals

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Abstract

Tristhiourea potassium chloride single crystals were grown by slow evaporation method under room temperature. The grown crystals were subjected to powder XRD analysis and confirm its structure and lattice parameters. The optical transparency of grown crystal was studied by UV-Visible spectroscopy and the molecular structure was confirmed by FTIR analysis. The thermal studies confirms the thermal stability.

Keywords: *Crystal growth, XRD, SEM, NLO, Dielectric constant*

INTRODUCTION

Non Linear Optical (NLO) materials find a variety of applications such as frequency conversion, light modulation, optical switching, optical memory devices and optical second harmonic Generation (SHG) [1-5]. The higher chemical stability and economic viability with good kinetic growth properties have made to pay attention on them in past decades. As a result, very good semi organic NLO material have been developed and are found to be suitable for a number of applications [6,7]. Many authors have used some techniques for a variety of materials characterisations. As for the metallic part focus is on the group II B metals (Zn, Cd, Hg) usually have high transparency in uv region because of their closed d^{10} shell. Potential NLO materials like bis thiourea cadmium chloride (BTCC), Trially thiourea Cadmium chloride (TATCC) [8] are examples of this approach in which the addition of some metal ions is expected to influence the growth kinetics, habit modification and the large size single crystal. The presence of small amount of impurities plays an important role in the growth rate, habit modification of the crystal and its chemical properties [9].

EXPERIMENT

In this present work the method used to grow crystals was slow evaporation method. Tristhiourea potassium chloride can be grown from aqueous solution by slow cooling and slow evaporation method. The Tristhiourea potassium chloride was prepared by mixing potassium chloride and thiourea in the stochiometric ratio 1:3 in deionized water in room temperature. To prepare Tris thiourea potassium chloride, 20ml of deionized water is taken in a beaker. To this, first add the amount of thiourea and completely stir it. When thiourea is completely dissolved, add potassium chloride to it and stir well. After complete dissolution of solutes in solvent, the mixture was heated with constant stirring followed by slow evaporation of solution at room temperature for getting good and homogeneous yield of Tristhiourea potassium chloride.The product was further purified by repeated crystallization. Growth was carried out by low temperature solution growth technique by slow cooling. The solution is then kept in room temperature. The solution containing beaker is covered with perforated filter paper to promote slow evaporation. This chapter deals with the result and its interpretation obtained from the analysis of tristhiourea potassium chloride. The analysis carried out for this present study are X-ray diffraction , FTIR, UV –Visible , SEM, EDAX and Thermal analysis etc. The results of all these studies are presented and discussed. The photograph of growing crystal is shown below.

Figure 1. Photograph of grown crystal

RESULTS AND DISCUSSIONS

XRD Analysis

Fig.2 shows the X-ray diffraction pattern of tris thiourea potassium chloride crystals. Exhibited peaks at definite angular location manifest the phase purity and also the poly-crystalline nature of the samples. Highly intense peaks without any additional peaks of impurities obviously state the phase purity of material. The broadening of these diffraction peaks indicates that the size of the crystal is very fine. In order to determine the crystal structure and to extract the structural parameters of the product , XRD study was carried out on a Philips X pert pro with CU Kα radiaton (=1.54056A) for the phase analysis . The powdered samples were scanned over the range of 2θ (10 – 70) with an angular step of 0.02°/min. XRD spectrum of Tristhiourea potassium chloride has a number of good intensity peaks at specific 2θ values. This shows high crystallinity of the grown crystals. The lattice parameters of tristhiourea potassium chloride calculations are a =7.565A^0, b =7.254A^0, c =6.69A^0, α=β=γ=90° which shows the orthorhombic crystal structure.

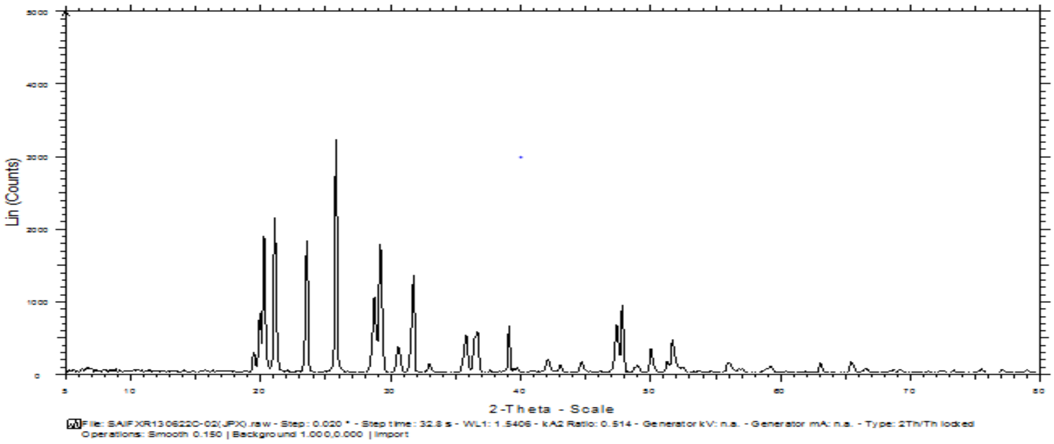

Figure 2. XRD spectrum of tris thiourea potassium chloride

FTIR techniques

FTIR spectrum of tristhiourea potassium chloride recorded using Perkin Elmer RXI spectrophotometer by KBr pellet technique in the range of 400-4000cm^{-1}. The spectra have a board envelop lying between 2750-3500cm^{-1} arising out of the symmetric and asymmetric modes of NH^{2+} group co-ordinated with thiourea. The presence of Cl^{-} ions is evident by its peak around 730cm^{-1} . The presence of additional peaks is lower frequency region around 500cm^{-1} to 1100cm^{-1} clearly confirms the presence of K^{+} ion in the co-ordinated sphere. C=S Stretching vibration occurs at 1413cm^{-1}. From the spectrum range 2700cm^{-1} -1800cm^{-1}nm have high percentage of transmission exists which is used for NLO applications.

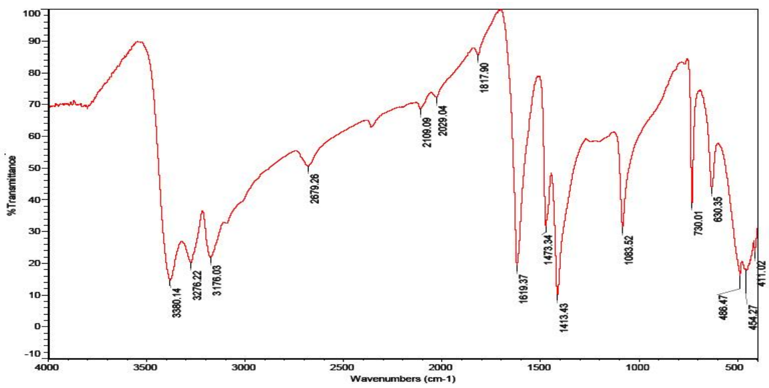

Figure 3. FTIR Spectrum of TrisThiourea Potassium Chloride

UV visible spectroscopy.

The UV –visible study of Tristhiourea potassium chloride are carried out by varian , cary 5000 model, UV visible spectrometer in the spectral range 200 nm -1100 nm. To cover entire near ultraviolet, visible and higher energy part of near IR region to know the suitability for non –linear optic applications , the spectral range is chosen in between 200 nm -1100 nm. The UV-Visible spectra of Tristhiourea potassium chloride crystals are shown in the following figure. The tristhiourea potassium chloride shows that the low UV cut off is at 330 nm. The optimized tristhiourea potassium chloride have band gap energy is 4.055 ev. The low uv transparency cut off wavelength is one of the essential requirements which make the tristhiourea potassium chloride suitable for frequency doubling.

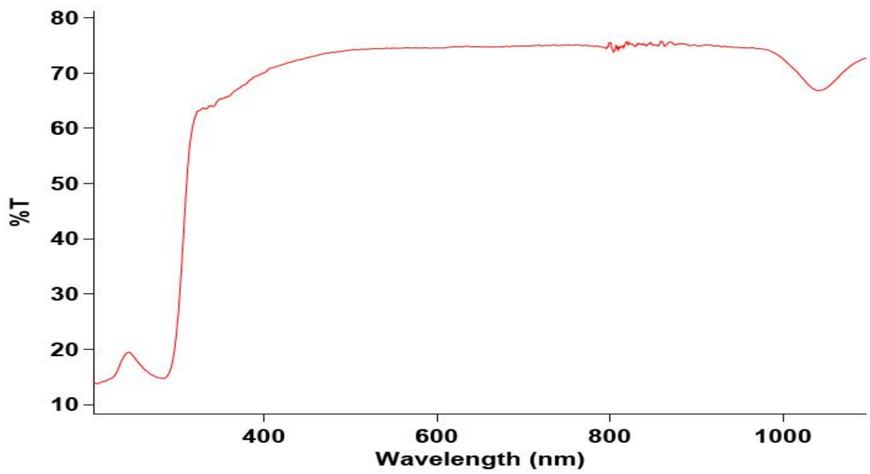

Figure 4: UV spectrum of tristhiourea potassium chloride

SEM ANALYSIS

SEM images recorded for three different magnifications x1500, x5000 and x10,000 revealed the morphology and size distribution of tristhiourea potassium chloride samples are shown in Fig . It is obvious that the size and morphology of crystals are different. The SEM images show a uniformly developed grain morphology of dense microstructure. The detailed examination of SEM micrograph from a selected region of tristhiourea potassium chloride indicates that these crystals are irregularly shaped. The size distribution and size of the particles are not uniform. The grain size varies from 1µm to 10µm. The obtained tristhiourea potassium chloride samples are very fine and agglomerated.

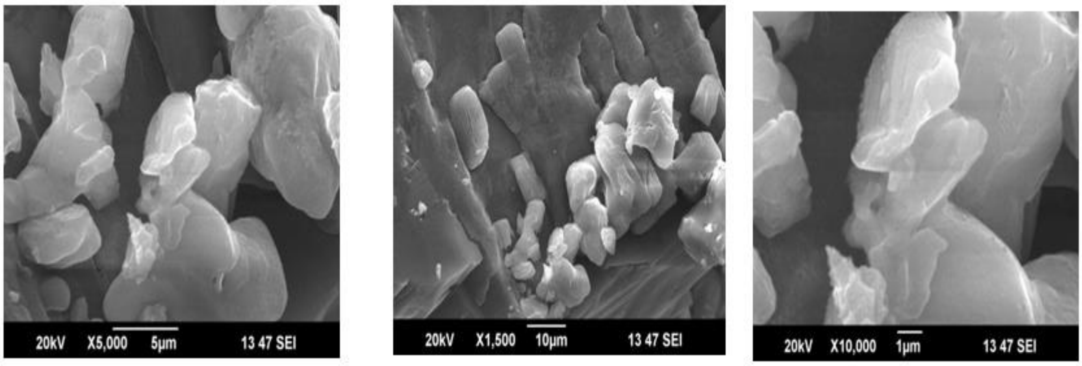

Figure 5. SEM images of tristhiourea potassium chloride .

EDAX

Fig shows the energy dispersive spectra of tristhiourea potassium chloride samples, the result indicates the presence C,N,S elements in the tristhiourea potassium chloride samples. The presence of hydrogen cannot be detected by EDAX measurement. The table gives the composition of all the elements and the percentage of atoms present in each compound. so it was clear that the N,S,C ions are present in the crystals.

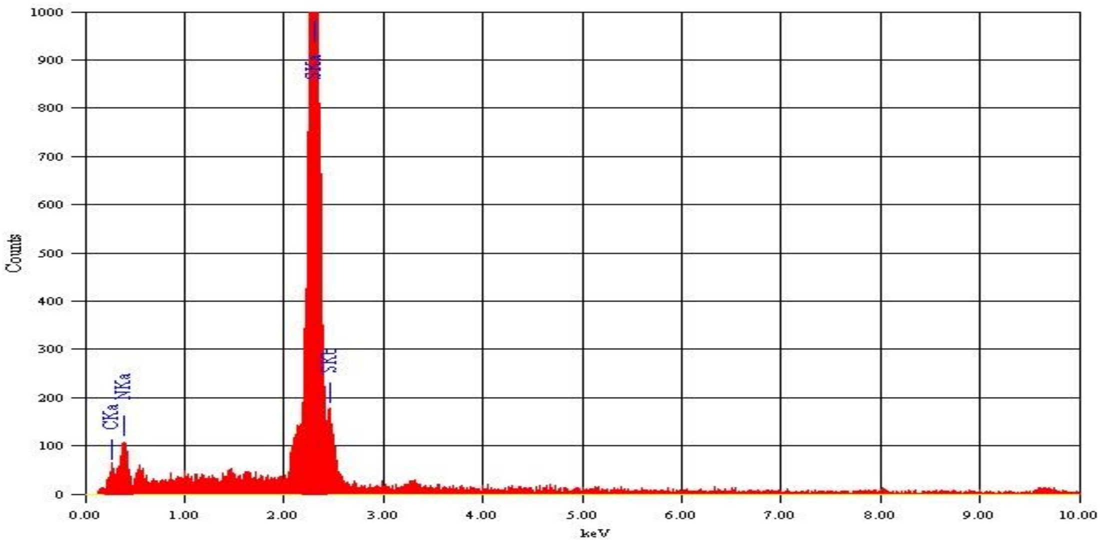

Figure 6. EDAX images of tristhiourea potassium chloride

THERMAL STUDIES

Thermal stability is an important parameter, acrystal should possess. Based on the range up to which the crystal is thermally stable its device application are decided. The TG/DT analysis are the familiar thermal technique to find the thermal stability and to identify the various transition (exothermic and endothermic) of a substance. The TG/DT analysis ware carried out using perkin Elmer Thermal analyser . The thermal analysis was carried out in the nitrogen atmosphere at a heating rate of 283k/min for the temperature range of 303-1093k .

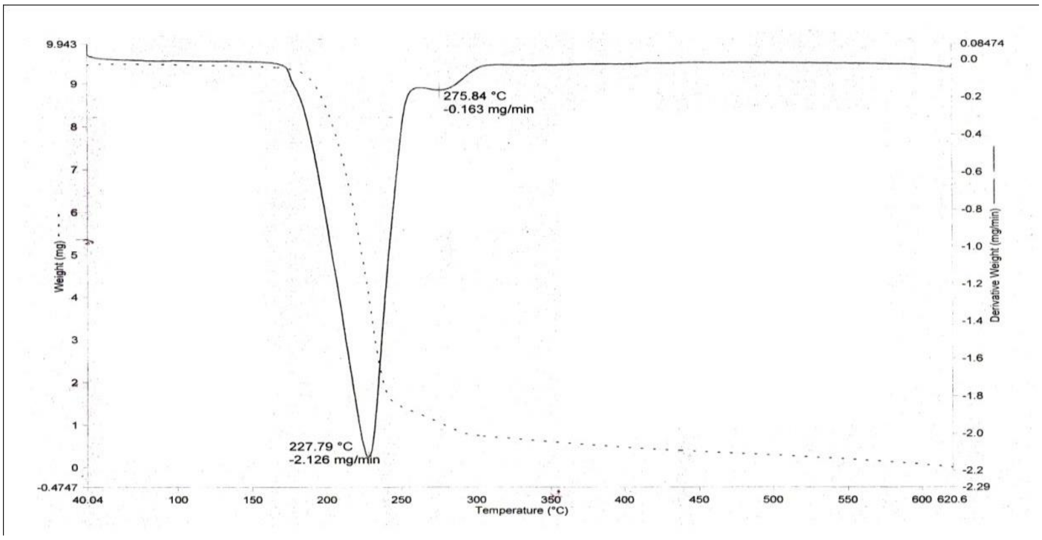

Figure 7. TGA/DTA curves of Tristhiourea potassium chloride crystal

Fig.7 show TGA/DTA spectra for Tristhiourea potassium chloride crystal. The curve exhibits mass losses in a single stage indicates that decomposition of the grown crystals takes place sharply. It is seen that the TG curve shows a plateaus upto 227.79C° suggesting that the compound is thermally stable upto a temperature of 227.79C°. After this temperature, the curve describes a mass loss of -0.163 mg/min upto 275.84C°. It is clearly seen in DTA curve, where there is a sharp endothermic peak at 233.14C° without any intermediate stages which is assigned as the melting point of the crystal.

CONCLUSION

The tristhiourea potassium chloride crystals are grown which are transparent and colourless. The tristhiourea potassium chloride crystals were carried out by the X- ray analysis. From this studies, the cell parameter and cell volume were calculated. Obtained tristhiourea potassium chloride has a orthorhombic structure. The product is analysed and characterized by XRD for its structural confirmation are purity. The presence of various functional groups of the grown crystals have been identified by FTIR spectral analysis. From the spectrum range 2700-1800nm high percentage of transmission exists which is used for NLO applications. Optical absorption studies were carried out using UV- Vis-NIR spectrophotometer and the related parameter, optical band gap energy was calculated. The UV spectral study reveals that the material has a wide optical transparency window in the entire region with a lower out off at 204nm. SEM clearly indicates that the tristhiourea potassium chloride particles are agglomerated in nature and are not single particles. The irregular shaped non-uniformly distributed particles of tristhiourea potassium chloride were confirmed using SEM micrograph. Energy dispersive analysis by x-ray (EDAX) was used to investigate the chemical composition of the prepared samples.

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