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Structural, Optical and Thermal Properties of Urea Thiourea Lithium Sulphate Crystal

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ABSTRACT

Lithium sulphate doped urea thiourea crystals were grown by slow evaporation method at 30 °C. The method of growing 1:3:2 UTLS crystals is explained. The structural studies on the grown crystals were carried out by X-ray diffraction analysis. The grown crystals are found to be in orthorhombic structure and the lattice parameters of pure urea thiourea crystal are a =7.657 Å, b = 8.588 Å and c= 5.485 Å. The lattice parameter is distorted due to the incorporation of lithium ion into the lattice sites of the urea thiourea crystal. The functional groups of the grown crystals have been identified by the Fourier Transform Infrared Spectroscopy. Optical transmittance and thermal stability of the materials were carried out by UV-Vis-NIR and TG/DTA analysis. The nonlinear nature of the crystal is confirmed by SHG test.

Introduction

Crystallization of organic materials for using non-linear optical devices is of greater importance. The extensive use of thiourea semi crystals in industries, modulators, electro optic and acoustic devices is due to its structural character. Lithium has the property of binding due to neutral paring. Also, the lithium water reaction is brisk and non-violent.

Lithium when mixed with sulphate acts as a very good soluble material. Lithium sulphate is monoclinic in structure and possesses a moderate melting point. All these alkaline salts have a tendency to have an easy bonding, since it has one free electron in the outermost orbit. With this in view, it has been proposed to mix this lithium sulphate in concentration of 2M with 1:3 UTLS and grow mixed crystal using slow evaporation method and characterize them.

To find its suitability as a better alternative to other NLO materials and for optoelectronics applications, the grown crystals were characterized by various techniques, such as Single and Powder XRD, FT-IR studies, UV Transmittance studies, TGA/DTA and SHG test analysis. These results are reported in this paper.

Materials and Methods

Synthesis and Crystal growth

To grow crystal of UTLS, Recrystallized UTLS salts were synthesized by dissolving urea, thiourea and Lithium sulphate in molar range (1:3:2) by mixing in double distilled water at 30 °C. The beakers containing the solutions were mixed thoroughly using a magnetic stirrer constantly for 6 hrs and were filtered using Whatman filter paper at the saturated solutions were covered with a paper and left undisturbed for slow evaporation using a constant temperature bath. The synthesized substances were purified by evaporation technique. Well developed, good transparent seed crystals were harvested in a growth period of less than 15 days. Selected seed crystals were fixed with the help of thread and again immersed in the saturated solutions are left undisturbed in a constant temperature bath. After a sufficient time of say 30 days good crystals were harvested and dimensions values are measured. The photograph of such crystal is shown in figure 1.

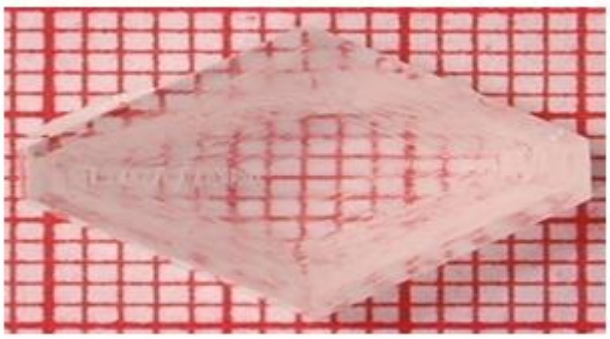

Figure 1. Photograph of UTLS crystal

Results and Discussion

Single Crystal X-ray Diffraction Study

X-ray diffraction is now a common technique for the study of crystal structure and atomic spacing. The grown UTLS crystal was subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD4 diffractometer with MoK_α radiation (λ=0.71073Å) to determine the unit cell dimensions. The structures have been solved by the direct method and refined by the full matrix least square technique using SHELXL program. Single crystal XRD data of UTLS indicate that the cell parameters are a=7.662 Å, b=8.598 Å and c=5.505 Å, V=362.653 $Å^3$. Interfacial angles α°=90. 203, β°=89. 941 and γ°=90. 387. It was found that UTLS crystal belongs to orthorhombic system with a non-Centro symmetric space group $P2_12_12$ (Pasupathi and Philominathan 2012).

Powder X-ray Diffraction Study

The grown UTLS crystal was subjected to grinding using an agate pestle and mortar. After careful sample preparation it was scanned over the range (2θ) of 10 to 80° using X-PERT PRO

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with CuK_α radiation (λ=1.54060Å). The XRD pattern of the UTLS crystal is shown in figure 2. The obtained XRD pattern was analyzed using PROSZKI software package. The positions of the peaks were found to be in good harmony with the data available in JCPDS file. The results suggest that all the crystal belongs to orthorhombic system. The sharp and well defined observed peaks confirm the good crystalline nature of all the grown crystal. The evidenced sharp, intense peaks reveal that the crystallites are pure urea thiourea and lithium sulphate and dislocation free (Manimekalai et al 2012).

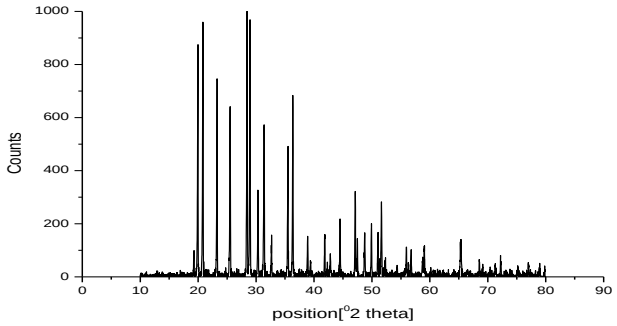

Figure 2. Powder X-ray Diffraction Pattern of UTLS Crystal

FT-IR Spectral Analysis

In order to analyze the grown crystal qualitatively for the presences of functional groups FT-IR spectrum was recorded between 4000-400 cm^{-1} using Perkin Elmer RXI FT-IR spectrometer, by KBr pellet technique. The recorded FT-IR spectra of UTLS crystal is shown in figure 3. In the FT-IR spectra of UTLS crystal, the broad envelope in between 3367 and 3165 cm^{-1} is due to the asymmetric and symmetric stretching modes of NH_2 group of thiourea molecules (Selvapandian et al 2013). The strong band observed around at 1589 cm^{-1} may be assigned to symmetric N-C-N bending. An observed band at 1463 cm^{-1} is due to asymmetric C-N stretching. A sharp peak at 1091 cm^{-1} is due to Symmetric C-N stretching compared to UTLS crystal. The asymmetric and symmetric C=S stretching of thiourea slightly shifted to a lower value than pure thiourea this is due to its co-ordinate interaction with metal ions in the frequency region at 1429 cm^{-1} and 729 cm^{-1} in UTLS crystal (Nalini Jayanthi et al 2013).

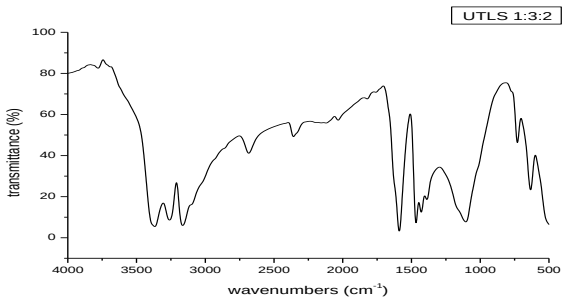

Figure 3. FTIR Spectra of UTLS Crystal

UV-Vis Study

The optical transmission spectrum of lithium sulphate doped urea thiourea of soluble crystal was recorded in the range 200 – 1100 nm using Shimadzu –UV 1800 spectrometer. A transmittance spectrum was recorded in the wavelength range of 200-1100 nm and is shown in figure 4. From the graph, it is observed that the crystal show good optical transmission in the entire visible and infrared region. At 258 nm a sharp fall of transmittance to zero was observed, indicating a single transition in the near UV region for UTLS crystal. Absence of absorption in the region between 300 nm to 900 nm is advantageous as it is a prime requirement for a material to possess NLO properties. The appearance of peak in the ultraviolet region may be attributed to the first overtone of N-H groups of strongly bonded hydrogen thiourea molecule (Manimekalai et al 2012).

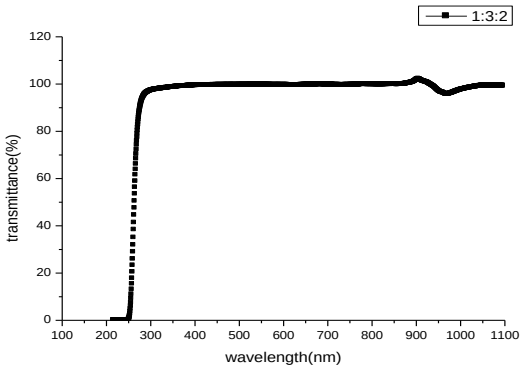

Figure 4. UV-Vis Transmittance Spectra of UTLS Crystal

Second Harmonic Generation Study

To find the nonlinear optical efficiency the second harmonic generation behavior of the powder UTLS material was tested using the Kurtz and Perry method. Q-switched mode-locked Nd:YAG laser emitting 1.64 µm fundamental radiation is used as the source. The emission of green light (λ=532 nm) confirms the grown UTLS crystal is the best suitable candidate for NLO materials and optoelectronic applications. In urea thiourea, the higher dipole moment is due to the presence of the polar NH amine group (Thendral et al 2013). Lithium sulphate doped in urea thiourea increases, when nonlinear optical efficiency increases. A relative efficiency of is about 0.68 times less than that of KDP was observed.

Thermal Analysis

The Thermogravimetric (TG) and Differential thermal analysis (DTA) of UTLS crystal was carried out using a NETZSCH - STA 449 F3 JUPITER model thermal analyzer. Powdered samples were used for the analysis in the temperature range of 30 to 1200°C at a heating rate of 20 °C / min in a nitrogen atmosphere. The recorded thermogram is shown in figure 5. From TGA curve, it is observed that the weight loss start from 120°C. There is a 15% weight loss between 120°C and 200°C. This weight loss is due to the liberation of sulphur atom and water molecules. There is no weight loss below 120°C. This indicates that the crystal is devoid of any physically adsorbed water in it. The DTA curve shows a sharp endothermic peak at 600 °C and 820 °C suggesting the melting point of the crystal. This endothermic event trace is in good agreement with the studied TGA by Suveetha et al (2012).

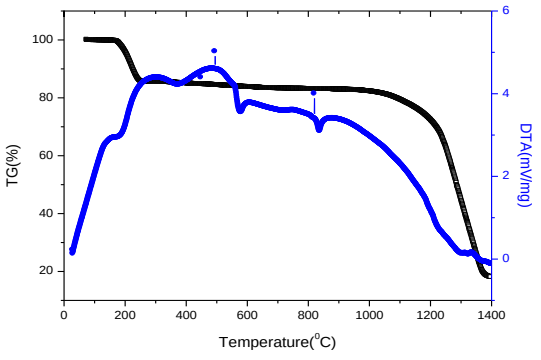

Figure 5. TG/DTA Curve of UTLS Crystal

Conclusions

Optically good quality crystal of UTLS was grown by slow evaporation technique at 30 °C within a period of three weeks. The lattice parameters were determined from the single crystal XRD and it has been found that UTLS belongs to the orthorhombic crystal system. The sharply well defined Bragg's peak confirms the crystalline nature of the grown UTLS crystal. It was confirmed by powder XRD pattern. The FT-IR is effectively used to identify the functional groups present and it has been found that stretching vibration of molecules at certain frequencies. The optical transparency and the lower cutoff wavelength at 258 nm were identified from the UV-Vis-NIR spectrum. The Kurtz powder second harmonic generation test show that the crystal is a promising candidate for optical second harmonic generation applications. Thermal analyzer reveals that the grown crystal was thermally stable up to 120 °C.

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