Available online at www.elixirpublishers.com (Elixir International Journal)

Crystal Research

Elixir Crystal Research 98 (2016) 42503-42505

ISSN: 2229-712X

Growth, Spectral, Optical, Thermal, Structural Properties of Urea Thiourea Potassium Sulphate Crystal

P. Saritha[1] and S. Barathan[2]

[1] Engineering Physics Section, Annamalai University, Annamalai nagar-608002, India.

[2]Department of Physics, Annamalai University, Annamalai nagar-608002, India.

ARTICLE INFO

Article history:

Received: 29 July 2016;

Received in revised form: 26 August 2016;

Accepted: 5 September 2016;

Keywords

FT-IR,

SHG,

SEM analysis,

Single and Powder XRD,

TG/DTA and UV-Vis.

ABSTRACT

The present paper reports the growth of Urea Thiourea Potassium Sulphate crystal (UTKS) by slow evaporation method at 30 °C. A Single and Powder X-ray diffraction analysis reveals that UTKS crystals belong to orthorhombic structure at various diffracting planes of the grown crystal were identified. In various functional groups of the grown UTKS crystal were identified by FT-IR spectral analysis. Optical transmittance and energy band gap of grown crystal have been measured from UV-Vis studies. Second harmonic generation was investigated to confirm the non-linear optical properties. The thermal behavior has been examined by TG/DTA analysis and the SEM images of the crystal reveal the well formation of the faces of the crystal.

Introduction

NLO materials play a significant part in the area of fiber optic communication, laser technology, optical signal processing, optoelectronics, telecommunication, and optical storage devices in all emerging fields of technology; many scientists focused their attention on the growth of NLO materials especially crystal. The orthorhombic crystal system is called as β- K_2SO_4. Potassium sulphate K_2SO_4 belongs to the orthorhombic system with space group Pmcn and with lattice parameters a=5.763Å, b=10.071Å and c=7.476Å (Frondel, 1950). The relative density is 2.662 g/cm^3. The melting point is at 1069˚C and the boiling point is at 1689˚C. In this study, an attempt is made to combine potassium sulphate doped urea thiourea mixed crystal UTKS for growing a new semi organic non-linear optical material by slow evaporation technique. Also, structural, vibrational, optical and thermal properties were explained.

2. Growth of Experimental Crystal

Crystal of UTKS was grown by the slow evaporation technique at 30 °C using double distilled water as solvent. The solutions were prepared by dissolving urea thiourea (1:3) and potassium sulphate doped urea thiourea in molar ratio of 1:3:2 in double distilled water at 30 °C. The filtered solutions were distributed into different beakers. The solution was stirred well for about 6 hours using a magnetic stirrer constantly. The saturated solutions were filtered using whatmann filter paper. The filtered solutions were poured into beaker and it is kept at constant temperature bath maintained at 30 °C in a dust free compartment for the slow evaporation process. The beaker was closed with a paper and the solution in the beaker was allowed to evaporate. After a few days small good optical transparent seed crystal started growing in the beaker. The grown crystal is selected for use as seed. The selected seed crystal was fixed with the help of thread and again immersed in the saturated solution undisturbed in a constant temperature bath. After three weeks of growth colorless very transparent crystal is obtained. This process is repeated till sufficient growth of crystal was obtained. The photograph of UTKS crystal is shown in Fig.1. The size of the grown crystal was measured for its dimensions (Kalaiselvan et al 2012).

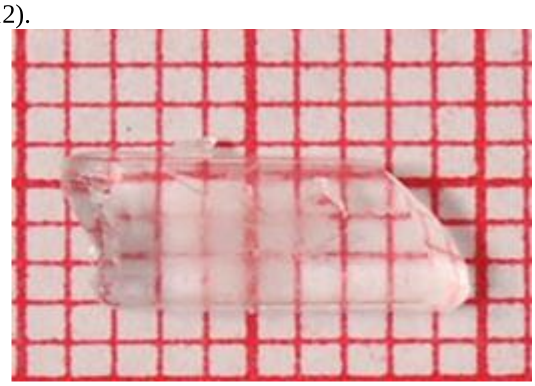

Figure 1. Photograph of UTKS crystal

3. Results and Discussion

3.1. Single Crystal X-ray Diffraction Study

Single crystal XRD data of potassium sulphate doped urea thiourea crystal was recorded using an ENRAF NONIUS CAD4 diffractometer with MoK_α radiation (λ=0.71073Å) to determine the unit cell dimensions. The structure has been solved by the direct method and refined by the full matrix least square technique using SHELXL programme. Interfacial angles α°=90.159, β°=90.008 and γ°=89.874. It was found that UTKS crystal belongs to orthorhombic system with a non-Centro symmetric space group $P2_12_12_1$. This change may be due to the presence of thiourea in potassium sulphate crystal (Radhika et al 2013). There are three axial unequal length a(Å) = 7.601, b(Å) = 8.540 and c(Å) = 5.483 and volume of the unit cell (V)= 355.916(Å^3) values have been determined.

3.2. Powder X-ray Diffraction Study

The powdered sample UTKS crystal was subjected to powder X-ray diffraction analysis and scanned over the range

Tele:

E-mail address: psarithaau@yahoo.com

(2θ) of 10 to 80 ^{o} using X-PERT PRO with CuKα radiation (λ=1.54060Å). The XRD pattern of the UTKS crystal was recorded and a spectrum is shown in Fig. 2. The obtained XRD pattern was analyzed using PROSZKI software package. Miller indices of the planes were calculated and Bragg's peaks have been indexed. The sharp and well defined peaks confirm the good crystalline nature of the grown UTKS crystal. These results are all most similar to the data available in JCPDS files (Marcus Aurelio Ribeiro mirando et al., 2006).

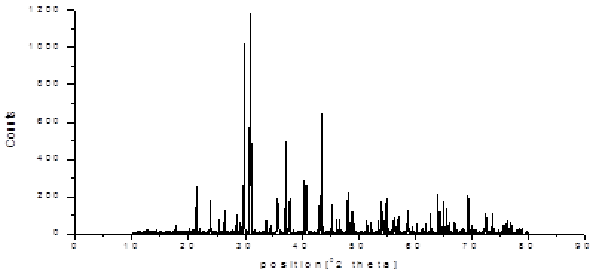

Figure 2. Powder Diffraction Pattern of UTKS Crystal

3.3. FTIR spectral Analysis

The functional groups were identified by Fourier transform infrared studies using Perkin Elmer RX1 FT-IR spectrometer in the range 4000 – 400 cm^{-1} KBr pellet technique was employed for recording the spectrum. The FTIR spectrum of UTKS crystal is shown in Fig. 3. The other characteristic Vibrational frequencies are assigned and tabulated Table 1. UTKS crystal vibrational frequencies were compared to urea thiourea. Thus decreasing the bond order of carbon-sulphur link towards the value of a single bond, while that of the carbon-nitrogen bond approaches the value of a double bond. Hence, in such complexes, the CS stretching frequency should be decrease and that of CN opposite effect is to be expected Ruby et al 2012.

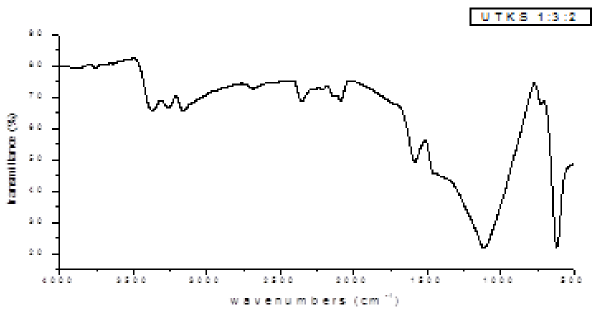

Figure 3. FTIR spectra of UTKS Crystal

Table 1. Vibrational Band Assignments of UTKS Crystal

UTU(1:3)	UTKS (1:3:2)	Assignments
3369	3369	Asymmetric NH_2 stretching
3259	3259	Symmetric NH_2 stretching
3161	3159	Symmetric NH_2 stretching
1585	1583	Symmetric N-C-N bending
1460	1448	Asymmetric C-N stretching
1091	1092	Symmetric C-N stretching
732	727	Symmetric C=S stretching
626	624	Asymmetric S-C-N bending

3.4. UV-Vis Study

An optical transmission spectrum was recorded using potassium sulphate doped urea thiourea crystal in the range of 200 to 1100 nm using Shimadzu-1800 spectrometer (UV-VIS-NIR). For optical device applications, the transmission spectrum is important, as the grown crystal can be used only in the highly transparent region. The UV transparency, lower cutoff wavelength for the grown crystal occurs at 285 nm (Fig.4). These observations well, coincide with other reported values for optoelectronic applications (Begum 2009). The energy band gap value of UTKS crystal is found to be 4.35 eV.

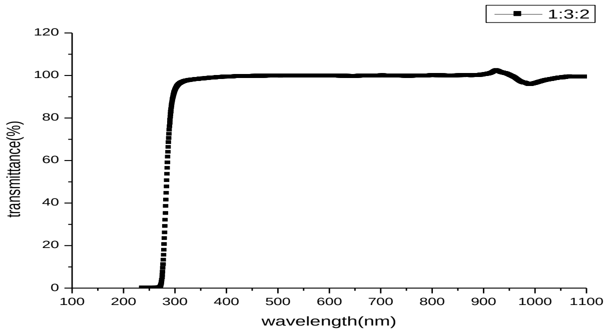

Figure 4. UV-Vis Transmittance Spectrum of UTKS Crystal

3.5. Second Harmonic Generation Study

The NLO efficiency of the crystal was evaluated by Kurtz and Perry Technique using a Q-Switched, mode logged Nd:YAG laser beam of wavelength 1064 nm (Quanta ray series) supplied by USA, Spectra Physics, Coherent electronic power meter. The second harmonic generation efficiency of the UTKS crystal was observed and found to be non-linear optical materials. Potassium dihydrogen orthophosphate (KDP) crystal was powdered to the identical size as that of experimental crystals and used as a reference material whose SHG efficiency is 8.8 mJ. The SHG efficiency for potassium sulphate doped urea thiourea crystal is found to be 0.51 times that of KDP sample and hence the sample is better candidates for NLO applications (Aruna et al 2007).

3.6. Thermal Analysis

Thermogravimetric analysis of the UTKS crystal was carried as a function of weight loss versus temperature using a NETZSCH - STA 449 F3 JUPITER model thermal analyzer. Powdered samples were used for the analysis in the temperature range of 30 to 1400 ^{o}C at a heating rate of 20 ^{o}C / min in a nitrogen atmosphere. TG/DTA curves of the UTKS crystal is shown in Fig 5. From TGA reported around the first no weight loss occurs up to 30 °C to 200 °C due to the removal of the hydrogen atom. The next stage of the weight loss of 4.2% are due to the after all decomposition of the residual material. Thus UTKS crystal was thermodynamically stable up to 200 °C. The decomposition temperature of thiourea which is 182 °C may be due to the formation of metal complex. From DTA curve, show a sharp endothermic peak at 1060 °C is due to the melting point of the UTKS crystal.

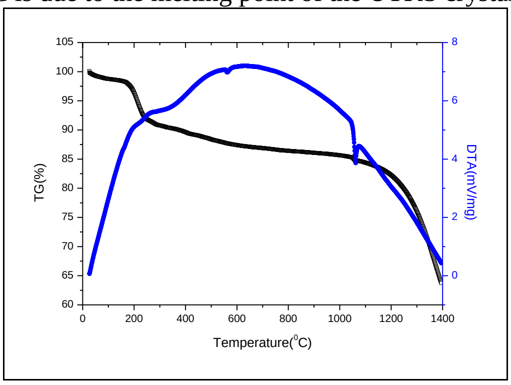

Figure 5. TG/DTA Curve of UTKS Crystal

3.7. SEM Analysis

SEM analysis was carried out using JEOL JSM-5610 LV Scanning Electron Microscope. The investigation of the influence of thiourea on the surface morphology of the UTKS crystal structure reveals the well formation of faces in crystal (Fig. 6). In the presence of thiourea in the growth medium, the SEM photograph of UTKS crystal show an orthorhombic structure (Thiyagaraj and Meenakshi 2012).

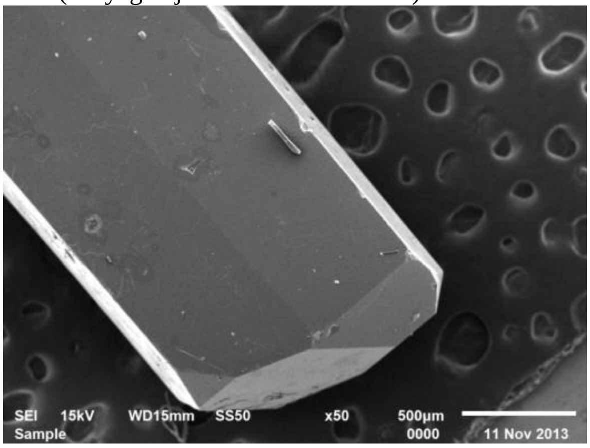

Figure 6. SEM Photograph of UTKS Crystal

4. Conclusion

Growth of urea thiourea potassium sulphate crystal (UTKS) was grown by the slow evaporation method. UTKS single crystal and powder XRD were found that the crystal belongs to orthorhombic system with non-Centro symmetric space group $P2_12_12$ and unit cell parameters and crystalline nature of the materials are determined. UTKS crystal vibrational band frequency assignments were compared to urea thiourea by FT-IR spectral analysis. Optical transmittance of the grown crystal has been measured from UV-Vis spectrum and the lower cutoff wavelength at 285 nm was identified. The SHG test was investigated to confirm the non-linear optical properties of the material. Using thermal analysis reveals that the grown crystal is thermal stability up to 200 °C. The SEM images of the UTKS crystal reveal the well formation of the faces of the crystal.

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