



Thermal, optical, mechanical and dielectric characterization of urea doped thiourea zinc sulphate single crystals

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ARTICLE INFO

Article history:

Received: 10 June 2013;

Received in revised form:

24 July 2013;

Accepted: 7 August 2013;

Keywords

Crystal growth;

FTIR;

TGA-DTA;

Micro hardness;

Dielectric study.

ABSTRACT

The organo-metallic nonlinear optical material urea doped thiourea zinc sulphate (UTZS) has been successfully grown by slow evaporation method at constant temperature 30°C from its aqueous solutions. The grown crystals were subjected to powder x-ray diffraction to determine the unit cell parameters. The UV-Vis transmittance spectrum shows that the crystal has a good optical transmittance in the entire visible region with lower cutoff wavelength. The second harmonic generation efficiency was measured in comparison with KDP by employing powder Kurtz method. The vibrational frequencies of various functional groups in the crystals have been derived from FI-IR analysis. The thermal stability of the grown crystal was analysed by thermogravimetric (TGA) and differential thermal (DTA) analyses. The vicker's hardness was carried out to test even distribution of load and to study the mechanical strength of the crystal. The dielectric response of the crystals was studied in the frequency range 100HZ-5MHZ at different temperatures and the results are discussed.

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Introduction

Nonlinear optical materials have received much attention due to their applications in high data storage, colour displays, laser technology, optical communications, optoelectronic technologies etc. [1-5]. In the recent past extensive investigations are being carried out on both organic and inorganic NLO materials. The high SHG efficiency in organic materials is due to the presence of delocalized π -electron systems connecting donor and acceptor groups which enhances the asymmetric polarizability. But their use is impeded by their low optical transparencies, poor mechanical stability, low laser damage threshold and inability to produce large size crystals. Inorganic nonlinear optical materials, on the other hand, have excellent mechanical and thermal properties but with modest optical nonlinearities because of the lack of extended π -electron delocalization [6, 7]. To overcome these problems, a new-class of organic-inorganic hybrid components called organo-metallics, have been introduced [8-13]. The recent search is concentrated on organo-metallic nlo materials due to their large non linearity, high resistance to laser induced damage and good mechanical hardness [14, 15]. In search of these semi organic NLO materials urea and urea analogs have been explored. Thiourea molecule has large dipole moment and forms an extensive network of hydrogen bonds. The centro-symmetric thiourea molecule when combined with inorganic salts yields non centro-symmetric complexes, which have nonlinear optical properties. Motivated by this consideration; a lot of thiourea complex crystals were grown and explored. A number of studies on metal coordination compounds of thiourea have been reported earlier [16-21].

In the present study attempts have been made to grow optically clear crystals of UTZS by slow evaporation method. The structural, thermal and optical characterizations of the grown crystals were then made by XRD, FTIR, UV-Vis, SHG, TGA, hardness and dielectric studies.

Crystal growth

Large single crystals can be grown from slow evaporation solution growth [22, 23]. Single crystals of urea doped thiourea zinc sulphate were grown by slow evaporation of the saturated aqueous solution at room temperature. Solutions were mixed about 5h using a magnetic stirrer to get homogeneous temperature and concentration throughout the volume. The saturated solution was filtered twice to remove the suspended impurities and collected in beakers and left undisturbed. Good quality single crystals were grown over a period of 30 days. The grown crystal is shown in Fig. 1.

Characterization

The crystalline nature of grown crystals of UTZS were confirmed by powder X-ray diffraction analysis using Philips Powder x-ray diffractometer. The functional groups were identified by Fourier Transform Infrared studies using BRUKER IFS 66V FTIR spectrometer in the range of 4000 – 400 cm^{-1} . The optical transmission spectrum is recorded using VARION spectrophotometer. The thermogravimetric analysis was performed using SDT Q 600 V 8.3 instrument. To confirm the nonlinear property, Kurtz powder SHG test was conducted. The dielectric constant and the dielectric loss of the UTZS sample were studied using HIOKI 3532-50 LCR HITESTER in the frequency range of 100Hz to 5 MHz.

Results and Discussion

Powder x-ray diffraction analysis

To confirm crystalline nature of the grown crystals and also to determine the unit cell parameters the x-ray diffraction analysis was carried out using the powder sample of UTZS. The sample was scanned over the range 20° to 60° at a scan rate of $1^\circ/\text{min}$. The x-ray intensity data of the powder sample UTZS is shown in Fig. 2. The unit cell dimensions were calculated from powder x-ray diffraction using PROSZKI software package [24]. The obtained crystallographic data are presented in the Table 1 and values are compared with single x-ray data of thiourea zinc sulphate from the literature [25].

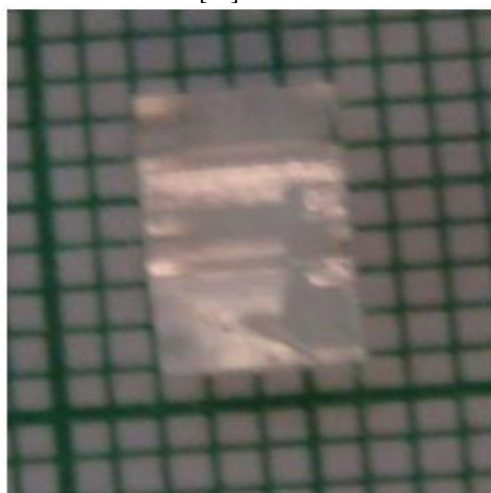


Fig. 1 Single crystal of UTZS grown by slow evaporation technique

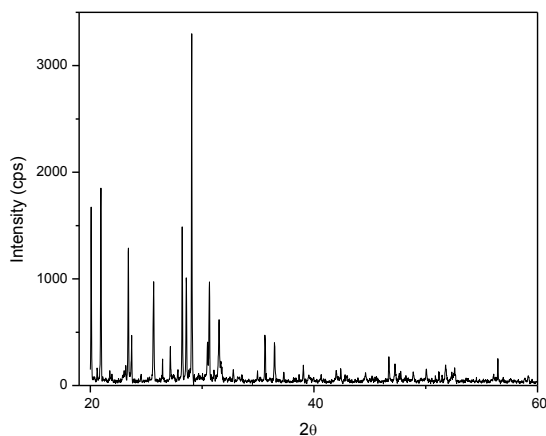


Fig. 2 The x-ray powder diffraction patterns of the crystals UTZS

UV-Vis spectral analysis

Efficient NLO crystals have an optical transparency lower cutoff wavelength between 200 and 400 nm. The transmission spectrum of the UTZS crystal is shown in Fig.3. The lower cut off wavelength of UTZS crystal is found to be 240 nm. From the UV-Vis spectral analysis it is clear that there is no significant absorption in the UV and visible region thereby confirming the advantages of the crystals, the large transmission in the entire visible region and short cut off wavelength enables the crystals to be useful for second and third harmonic generation of Nd:YAG laser fundamental.

SHG studies

Kurtz [26] second harmonic generation (SHG) test was performed to find the NLO property of the UTZS crystals. Kurtz technique is used as a screening technique to identify the materials with the capacity for phase matching in addition to identifying the materials with non Centro -symmetric crystal structure. The crystals were ground into powder and densely packed in between two glass slides. An Nd: YAG laser beam of pulse width 8 ns at a wavelength of 1064 nm and 10 Hz fundamental radiation was made to fall normally on the sample cell. The emission of green light confirms the second harmonic generation of the crystals. When a laser input of 6 mJ was passed through UTZS crystal second harmonic signal of 86 mV is produced and the experiment confirms a second harmonic efficiency of nearly 1.6 times that of KDP.

Fourier Transform Infrared (FTIR) analysis

The FTIR spectra of UTZS crystals are shown in Fig 4. The characteristic vibrational frequencies are assigned and compared with urea, thiourea and UTMS. [27,28]. The NH asymmetric and symmetric vibrational bands of thiourea has formed a broad envelope between 3400 cm^{-1} and 3100 cm^{-1} . The bands observed at 1617 cm^{-1} attributed to NH_2 deformation vibration. In pure thiourea C=S is bonded to NH_2 and the IR band for symmetric and asymmetric stretching vibrations of C=S group usually at 740 and 1417 cm^{-1} , but in UTZS, these vibrations are shifted to lower values of 730 cm^{-1} and 1413 cm^{-1} respectively. The shifting of C=S bonding to lower values and non shifting of NH_2 vibrations are due to the formation of metal sulphur bonds. So, on the basis of all available data of thiourea we have identified the characteristic IR bands for different molecular views present in UTZS. The peaks between 1700 and 2700 cm^{-1} were due to overtones and combination bands. The other characteristics vibrational wavenumbers are assigned in Table 2.

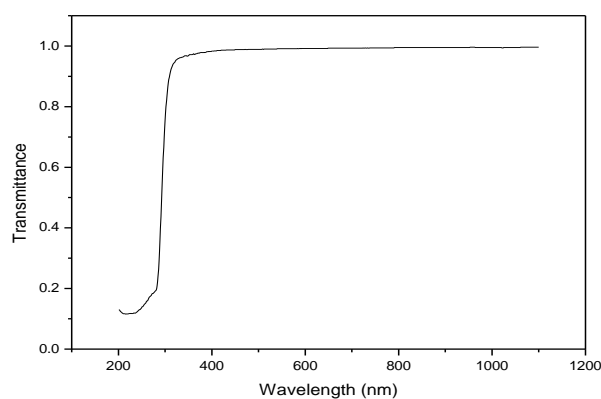


Fig 3. The transmission spectrum of the UTZS crystal

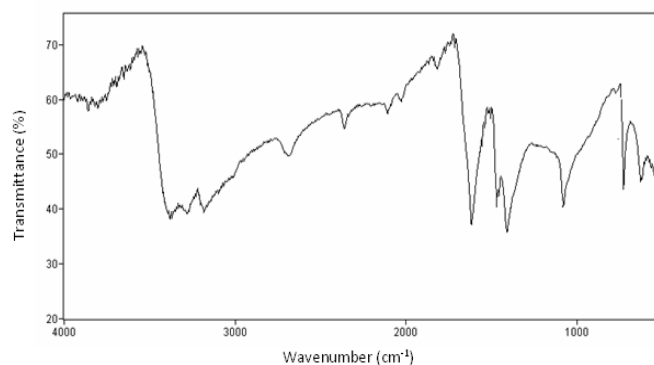


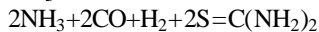
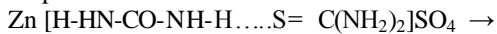
Fig. 4 The FTIR spectrum of UTZS crystals

Thermal analysis

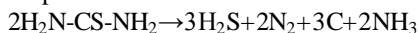
Thermal stability and physiochemical changes of the sample were analyzed by recording the TGA and DTA. Simultaneous TGA and DTA were carried out for the grown crystals in the temperature range of 28° C to 1100 ° C with a heating rate of 20K/min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in Fig. 5.

The following decomposition pattern is formulated for UTZS.

Step 1



Step 2



The absence of water of crystallization in the molecular structure is indicated by the absence of the weight loss around 100 ° C. Ramajothi et al [29] reported the melting point at 233 ° C of ZTS crystals (Tris thiourea zinc sulphate) and the decomposition of the crystals starts at 236 ° C. The sharp endothermic peak at 228 ° C is assigned to the melting point of UTZS crystals. The decomposition starts at 176° C and major weight loss occurs between 176° C and 243° C. Heavy mass loss and early decomposition indicates the presence of urea in UTZS. The UTZS crystal can be exploited up to 176° C. The high melting point of semi organic materials when compared with other organic crystals arises due to the stronger bonding existing between the conjugation layers of thiourea molecule and metal ion [30].

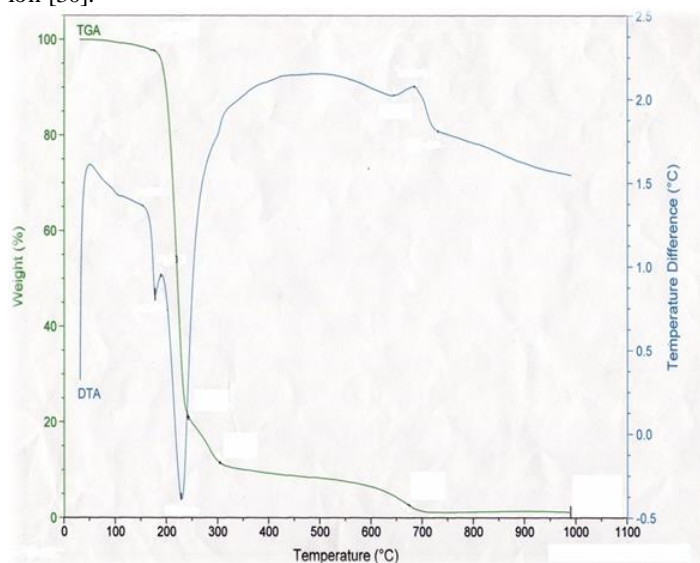


Fig. 5 The thermo gram and differential thermogram of UTZS crystals

Micro hardness Study

The mechanical properties of crystals are evaluated by mechanical testing which reveals certain mechanical characteristics. Among the different testing methods, the Vickers hardness test is more commonly used. Micro hardness measurements were made using Mututoyo MH 112 micro hardness tester. Vickers hardness indentations were made on the flat polished face of the crystals for loads varied from 10 to 50 gm for a reside period of 10s using Vickers diamond indenter attached to an incident light microscope. The Vickers hardness number $H_v = 1.8544P/d^2$ kg/mm² where P is the indenter load in kg and d is the diagonal length of the impression in mm. The variation of H_v with applied load is shown in Fig 6. The hardness number was found to increase with load. The work hardening coefficient (n) was found to be 1.52. The phenomenon

of dependence of microhardness of a solid on the applied load at low level of testing load is known as indentation size effect (ISE). The Mayer index number was calculated from Mayer's law [31], which relates the load and indentation diagonal length.

$$P = kd^n$$

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

where k is the material constant and n is Mayer's index (or work-hardening coefficient). The above relation with equation indicates that H_v should increase with P if $n < 2$ and decrease with P when $n > 2$. In order to calculate the value of 'n', the graph is plotted against log P vs log d (Fig. 7), which gives a straight line after least-square fitting: the slope of this straight line gives the value of n.[32] the photograph of Vicker's indenter for different loads are shown in Fig 8.

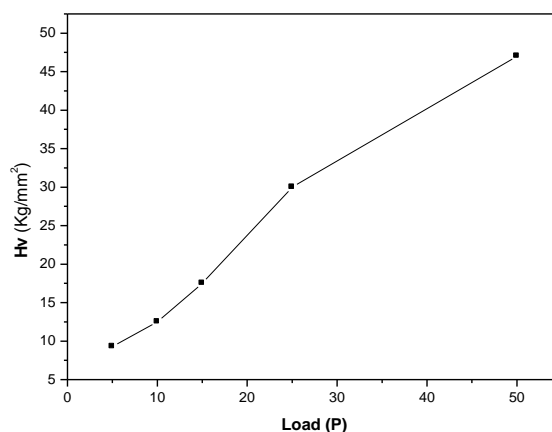


Fig 6. Variation of Vicker's Hardness Number (Hv) with Load (P)

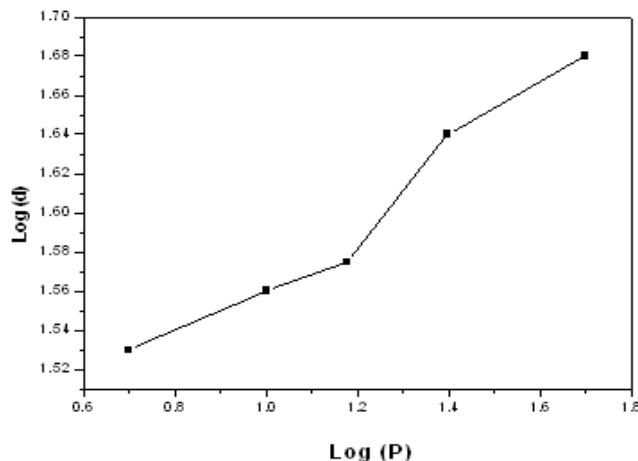


Fig 7. Plot between Log (P) Vs Log (d)



Fig 8. Photograph of Vicker's indenter

Dielectric studies

Fig. 9 shows the plot of dielectric constant as a function of log frequency and Fig.10 shows the plot of dielectric loss as a function of log frequency. The dielectric constant of the sample is calculated for varying frequencies under different temperature slots from 308 to 368 K.

Table 1: Crystal data of UTZS

Crystal Parameters	UTZS	TZS
a	5.7107	5.488
b	8.5188	8.591
c	7.5866	7.669
Volume (\AA^3)	369.074	365.066
α	90°	90°
β	90°	90°
γ	90°	90°
Crystal System	Orthorhombic	Orthorhombic
Space group	-	p2c2ab

Table 2: Comparison of Absorption IR bands

Urea	Thiourea	UTMS	UTZS	Assignments
	469			$\delta(\text{S-C-N})$
508	494	509	508	$\delta(\text{N-C-S})$
		631	629	$\rho(\text{C-H})$
	740	730	730	$\nu(\text{C-S})$
	1089	1083	1083	$\rho(\text{NH}_2)$
	1417	1412	1413	$\nu(\text{C=S})$
	1471	1473	1473	$\nu(\text{N-C-N})$
1631	1627	1621	1617	$\delta(\text{NH}_2)$
	3167	3178	3183	$\nu_s(\text{NH}_2)$
3320	3280	3283	3278	$\nu_s(\text{NH}_2)$
3422	3376	3388	3368	$\nu_{as}(\text{NH}_2)$

UTMS -Urea thiourea magnesium sulphate, UTZS -Urea thiourea zinc sulphate
 ν - Stretching, ρ - Rocking, δ - Bending
 ν_s - symmetric stretching, ν_{as} - asymmetric stretching

The dielectric constant value is higher at lower frequencies for all temperatures. The higher value of dielectric constant at low frequency compared to that at higher frequency is due to the presence of space charge polarization [33]. It is also observed that as the temperature increases, the value of dielectric constant also increases to a considerable value. The exchange of the charge carriers in the lattice sites is thermally activated by an increase in the temperature [34] resulting increase in dielectric constant. As the frequency increases both the dielectric constant and dielectric loss values are found to decrease exponentially and attain lower values. The dielectric constant becomes almost a constant over the wide range of frequency from 5 kHz to 5 MHz. The low value of dielectric constant explains the high SHG conversion efficiency of UTZS crystals and this in agreement with the Miller rule [35]. The low dielectric loss at higher frequency of the sample indicates that UTZS crystals possess lesser number of electrically active defects [36] and this parameter is of vital importance for non linear optical materials in their application.

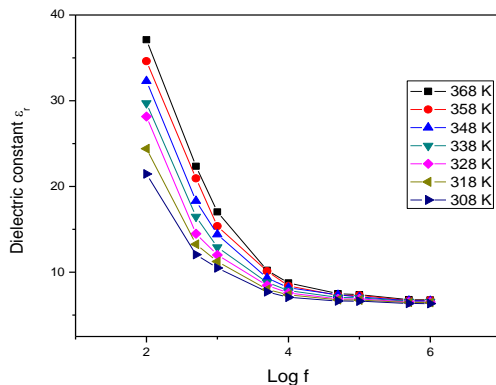


Fig 9. Dielectric constants Vs frequency

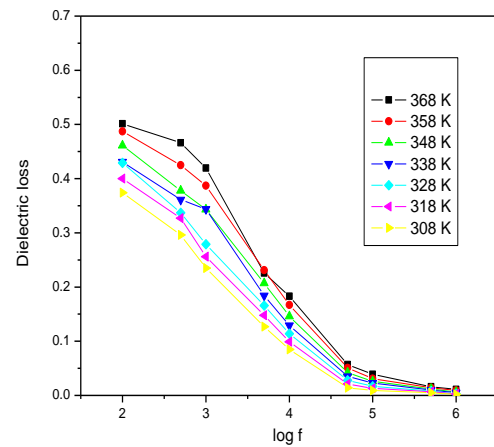


Fig 10. Dielectric loss Vs frequency

Conclusion

The good quality single crystals of UTZS were successfully grown by slow evaporation method at room temperature. The crystal structure has been determined by powder XRD analysis. Optical transmission studies show that the grown crystals were optically transparent even up to the NIR region. The second harmonic generation efficiency was measured by Kurtz powder technique using Nd:YAG laser and it is compared to that of KDP. The metal coordination with thiourea through sulphur is confirmed by FTIR analysis. TGA and DTA thermograms reveal the thermal stability of the sample. The n values are greater than 1.6, which shows that the UTZS crystals are fall under soft material category. The indentation impression shows these crystals have even distribution of load and have good mechanical strength. The variations in dielectric constant and dielectric loss were studied with varying frequency at different

temperatures. The low value of dielectric constant and dielectric loss combined with high SHG efficiency make the UTZS crystals are promising materials for laser applications.

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