

Synthesis and Characterization of Zirconyl Oxy Urea Thiourea Single Crystal Developed By Slow Evaporation Method

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Abstract: A single crystal of Zirconyl oxy urea thiourea has been grown successfully from its aqueous solution. The grown crystals have been subjected to X-ray diffraction studies to identify the morphology and structure. The TGA-DTA studies showed the thermal properties of the crystals. The functional group of the grown crystals was found by UV - Visible double beam spectra, FT-IR analysis, NMR and XRD studies.

Keywords: Urea, Thiourea, Zirconium Oxy-chloride, Zirconyl oxy urea thiourea (ZrOTU), X-Ray diffraction, UV-Vis, FT-IR, NMR, TGA, NLO and micro hardness.

I. Introduction

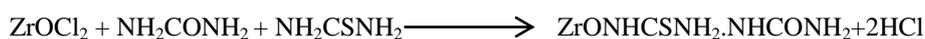
The formation of a single crystal structure in materials is affected by its atomic or ionic mobility behaviour. The pressure and temperature are the two major parameters that had been used gradually to control and adjust this mobility behaviour. Therefore, the crystal structure formation can be significantly affected temperature and external pressure. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications [1-10]. The major advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are essentially present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent developments in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Crystalline structure is more likely used in many applications compare to the non-crystalline structure. In this paper, the method of crystal growth with emphasis on low temperature solution growth technique was described.

II. Experimental Method

2.1 Synthesis

1g of urea, 9g of Thiourea and 5g of Zirconium Oxy-chloride were dissolved in 30 ml of double distilled water. The solution was thoroughly mixed using a magnetic stirrer. A crystalline substance was formed. The Urea Thiourea Zirconium Oxy-chloride solution was prepared in water and maintained at 30°C with continuous stirring to ensure homogeneous temperature and concentration. The solution was kept at 30°C for ten days in order to get hard thiourea and urea doped single crystal.

Crystal growth large single crystals can be grown from slow evaporation solution growth. Single crystals of Zirconyl oxy urea thiourea are grown by slow evaporation of the saturated aqueous solution at room temperature. Good quality single crystals were grown within ten days; the molecular structure and shape of the ZrOTU single crystal are shown in figure 1 and 2.



2.2 UV-Vis Spectral Analysis

The optical transmittance range and transparency cut-off wavelength are the main requirements for device applications.

2.3 Thermal Analysis

Thermo Gravimetric Analysis (TGA) gives the information regarding the phase transition and different stages of decomposition of the crystal system.

2.4 FT-IR Spectral Analysis

FT-IR Spectroscopic studies were effectively used to identify the functional groups present in the synthesized compound and to determine the molecular structure.

2.5 NMR

¹H NMR Chemical Shifts

Molecular structure of the grown crystal was investigated by ¹H NMR spectroscopy. The ¹H NMR spectrums indicate the presence of different proton environments in the title crystal.

¹³C NMR Chemical Shifts

¹³C NMR spectrum arises in the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied fields strength.

2.6 NLO Studies

Kurtz second harmonic generation (SHG) test was performed to find the NLO property of the ZrOTU single crystals. The crystals were ground into powder and densely packed in between two glass slides. A Q-Switched Nd: YAG laser beam of pulse width 8 ns at a wavelength of 1050 nm and 10 Hz fundamental radiation was made to fall normally on the sample cell and measurements were carried out.

2.7 Micro Hardness Studies

The mechanical strength of the grown crystal is estimated by Vicker's micro hardness test.

III. Results And Discussion

3.1. X-Ray Diffraction Analysis

Single crystal X-ray diffraction study was performed for the grown ZrOTU crystal. It was found that ZrOTU crystal belongs to orthorhombic system ($\alpha = \beta = \gamma = 90^\circ$). Lattice parameter values of ZrOTU are compared with reported TU shown in table 1. In the case of doped sample, a slight variation in the cell parameters is observed, which may be due to the incorporation of urea and thiourea ligands. This analysis revealed that the induction of urea and thiourea ligand in the ZrOTU crystal does not change the crystal system though there is a small change in the lattice parameters. The powder sample of ZrOTU was scanned over the range 10-80° at a rate of 1° per minute and the powder X-ray diffraction patterns were indexed using Check cell software (figure. 3). The Lattice parameter (a) was calculated by selecting the (102) plane using the formula [2].

$$\sin^2\theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

3.2. Fourier Transforms Infrared Spectroscopy

The FTIR spectra of Zirconyl oxy urea thiourea grown crystals are shown in figure 4. In the higher wavelength region, the peak at 3500 cm⁻¹ is assigned to C-H, N-H stretching vibration. The region 3500 cm⁻¹ and 3123 cm⁻¹ with strong intensity represents N-H stretching mode. The broad envelope positioned in between 3490 cm⁻¹ and 2711 cm⁻¹ corresponds to the symmetric and asymmetric stretching modes of NH₂ group. The peak at 2995 - 2900 cm⁻¹ with medium intensity refers C-H asymmetric stretching. Combinational overtones extend to the bands from 2300 - 2350 cm⁻¹. The peak at 1750 cm⁻¹ indicating the C=O stretching mode of vibration. The NH₂ bending vibrations occur at 1628, 1613 and 800 cm⁻¹. The peak at 1520 cm⁻¹ is due to NH₂ bending vibration. The peaks at 1420-1400 cm⁻¹ corresponds to the C=S stretching. The C-C stretching mode of vibration occurs in 1350 cm⁻¹ peak. The peak at 1215 cm⁻¹ gives rise to C-N stretching mode of vibration. The spectra show absorption bands in the region of 1160 cm⁻¹ and 1058 cm⁻¹ which are due to in-plane C-H bending vibration. The band 1120 cm⁻¹ signifies the N-H symmetric bending. The bands at 850 cm⁻¹ and 805 cm⁻¹ revealed that C-N deformation mode. The ring deformation occurs the peak at 820 cm⁻¹. C=O deformation is identified by the band at 690 cm⁻¹. C-H out-of plane bending peaks obtained at 660 cm⁻¹ and 648 cm⁻¹. The bands 655-638 cm⁻¹ represents C-C deformation. The absorption bands in the region of 486-471 cm⁻¹ are due to N-C stretching vibration. The assignments confirm the presence of various functional groups present in the material. The absorption around 1620 cm⁻¹ is NH₂ bending and this band would be shifted into lower wavelength region 1628 cm⁻¹. Our investigations were well compared with earlier reports [10-19]. The FT-IR spectrum data's are shown in table 2.

3.3 UV- Visible Studies

The UV-Visible spectrum of the single crystal ZrOTU shown in table 3 indicates Low absorption in the entire visible and near infrared region of the crystals. This is a desirable property for NLO applications since a wider optical transparency in these regions enhances the frequency conversion efficiency in the corresponding wavelengths. The lower cut off wavelengths of ZrOTU single crystal were found to be 275 nm, 279 nm and 315 nm respectively. The good optical transmittance in the entire visible region and the lower cut off wavelength (λ_{cut}) was observed as this is due to π - π^* transition in the compounds. The band gap energy ($E_g = hc/\lambda$) was found to be 4.95 eV for pure and Zirconyl oxy urea thiourea crystals. The large transmission in the entire visible region and short cut off wavelength enables it to be a potential material for second and third harmonic generation [20-25].

3.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectrum of ZrOTU was recorded using FT-NMR spectrometer. ZrOTU crystal was powdered and dissolved in deuterated dimethyl sulfoxide (DMSO). FT-NMR spectrum recorded for ZrOTU is shown in figure 5. A chemical shift at 7.5 – 7.6 ppm is due to =C-NH proton. The chemical shift at 7.06 ppm is assigned to =C-NH proton. Chemical shift at 2.511 ppm is due to –C=O. A chemical shift at 1.16 ppm is due to =C-proton [12]. The chemical shift at 7.742-7.763 is due to H–N–C=O. A chemical shift at 3.79 is due to –C=S. The above values confirm the structure of ZrOTU.

3.5 Thermal Analysis

TGA analysis of the ZrOTU crystal was carried out in the temperature range 10- 900°C. The recorded thermogram is shown in figure 6. From TGA curve it is observed that the weight loss start from 70°C. There is 16.5 % weight loss between 70°C. This weight loss is due to the liberation of HCl molecule. There is 11.9 % weight loss between 320°C and 350°C. This weight loss is due to the liberation of NH₃. There is 17% weight loss between 575°C and 690°C. This weight loss is due to the liberation of CO. There is 25 % weight loss between 850°C. This weight loss is due to the liberation of H₂S. This endothermic event is in good agreement with the TGA trace [21].

3.6 Micro Hardness Studies

Hardness of the material is a measure of resistance that offers to deformation. The transparent polished crystal free from cracks was selected for hardness measurements. The indentations were made on the flat surface with the load ranging from 25 to 100 g using Shimadzu make-model-HMV-2 fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vicker's hardness (Hv) was calculated from the relation [21],

$$Hv = \frac{1.8544P}{d^2} \quad P/d^2 \text{ kg/mm}^2$$

Where, P is the applied load and d the average length of the diagonal of the indentation mark. With P in g and d in μm , the units of Hv turned out to be kg/mm^2 . The variation of micro hardness with applied load for the prominent (102) plane of the ZrOTU crystal is shown in figure 7. It is found that the hardness values increases with the increase of the applied load. This behaviour of increasing micro hardness with the load known as reverse indentation size effect (RISE) [21], which is also attributed due to existence of distorted zone near crystal medium interface, effect of vibrations, specimen chipping etc., and the plastic deformation is dominant. At low loads or strains, plastic deformation of crystals mainly involves the nucleation of dislocations along a particular slip system. The RISE effect can be qualitatively explained on the basis of the depth of penetration of the indenter [21]. At small loads, the indenter penetrates only the surface layers and therefore, the effect is shown sharply at the early stages. When the applied load increases, the penetration depth also increases and the overall effect must be due to the surface and inner layers. When only one slip system is active during plastic deformation at low loads, the number of active parallel glide planes during indentation is low. Therefore the nucleating dislocations rapidly propagate into the material without experiencing substantial mutual interaction stress between them. Consequently in this stage, indentation depth increases proportionally with applied pressure.

3.7 NLO Studies

The second harmonic signal, generated in the crystals was confirmed from the emission of green radiation by the crystals. The NLO SHG values of the ZrOTU single crystals were determined and compared to the reported SHG value of pure KDP shown in table 4 [21-27].

IV. Conclusion

The good quality single crystals of Zirconyl oxy urea thiourea are successfully grown by slow evaporation method at room temperature. The UV-Vis spectra showed that the crystals had a wide optical window, no absorbance and good optical transmittance in the entire visible region. FT -IR analysis confirmed the presence of functional groups in the grown crystals. TGA thermo gram revealed the thermal stability of the materials. The powder X-Ray diffraction study confirms the lattice parameter values. The good optical quality and their suitability for NLO applications. Kurtz-Perry powder SHG test was employed to determine the SHG efficiency of the samples and the values were compared to the reported SHG efficiency of pure KDP.

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Table: 1 Comparison values of lattice parameter for the ZROTU crystal

Sample	System	2θ (degree)	FWHM	hkl	Lattice parameter (Å)	
					Calculated	Reference
TU	Orthorhombic	23.25	0.16	200	7.644	7.644
		20.81	0.16	020	8.527	8.559
		32.57	0.24	002	5.493	5.492
ZrOTU	Orthorhombic	23.26	0.39	200	3.821	3.821
		20.83	0.42	020	4.260	4.278
		28.50	0.48	002	3.129	3.356

Table: 2-IR Spectrum data's

Crystal	Wavenumber (cm ⁻¹)	Band Assignment
ZrOTU single Crystal	3500	C-H, N-H
	3500 and 3123	N-H
	3490 and 2711	NH ₂
	2995 - 3000	C-H
	1750	-C=O

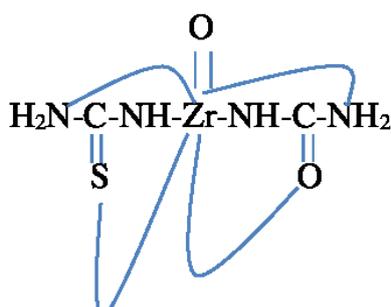
	1420 - 1470	-C=S
	1350	-C-C-
	1215	-C-N-

Table: 3 UV-Visible spectrum data's

Crystal	Wavelength (nm)	% Transmittance
ZrOTU	275	117.2
	279	98.5
	315	99.7

Table: 4 The NLO SHG value of ZrOTU single Crystal

Crystal	Second harmonic signal output (mJ)	SHG efficiency (compared to SHG efficiency of pure KDP)
ZrOTU	6.8	2.05



(Fig.1-Molecular structure of ZrOTU single crystal)



Fig.2-Shape of the (ZrOTU) single crystal

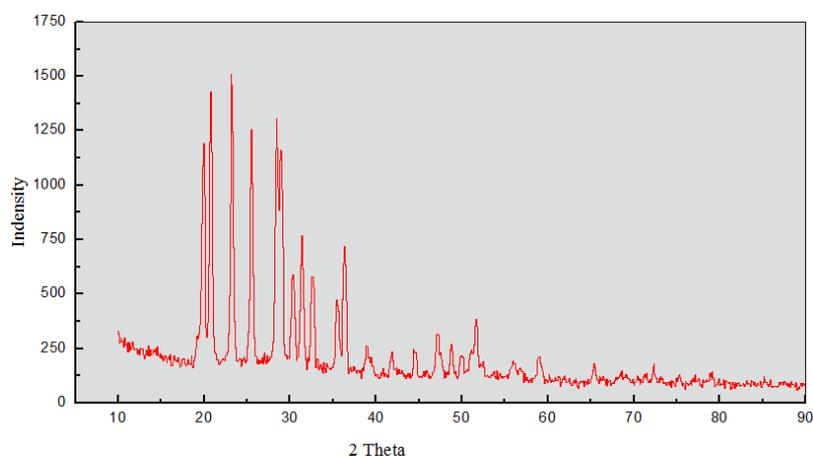


Fig.3- XRD pattern of the ZrOTU single crystal

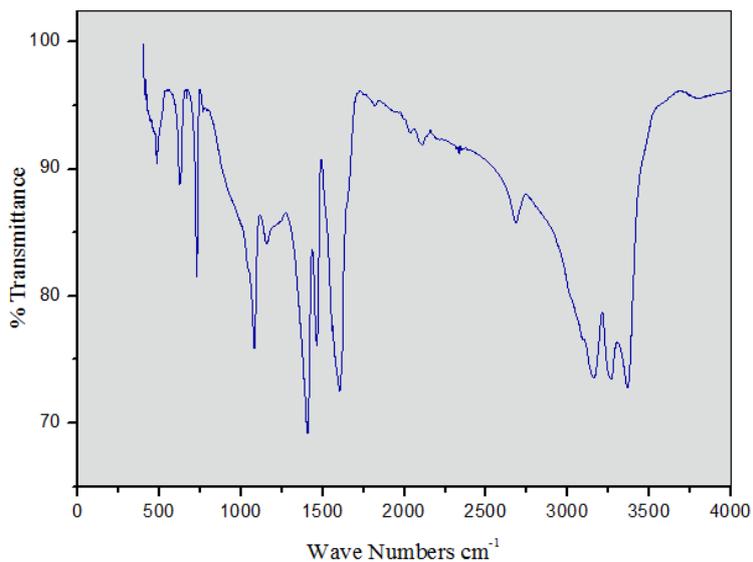


Fig.4-FT-IR spectrum of the ZrOTU single crystal

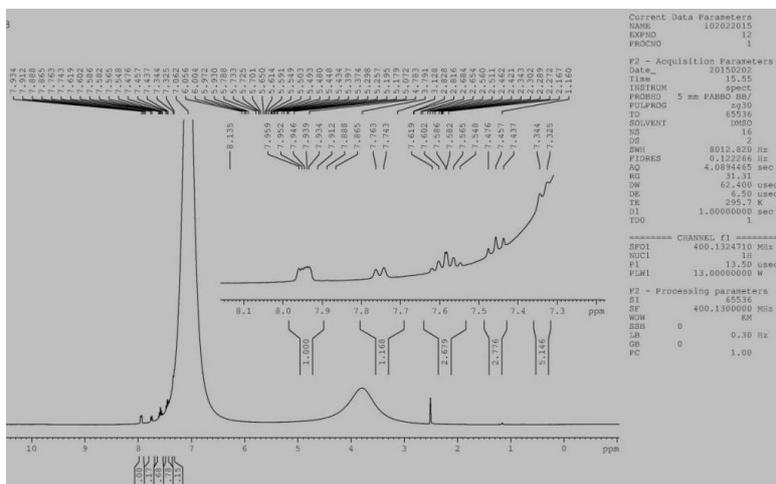


Fig.5 - NMR spectrum of the ZrOTU single crystal

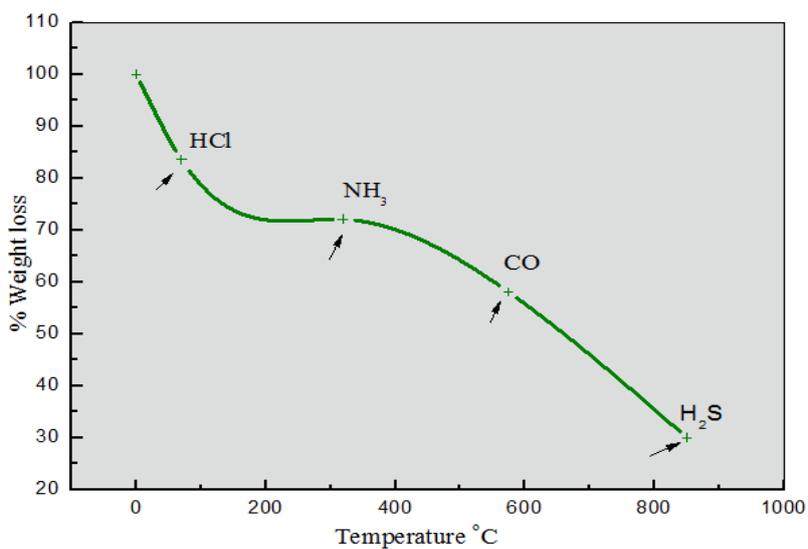


Fig. 6 - Thermo gravimetric analysis for the determining the weight loss

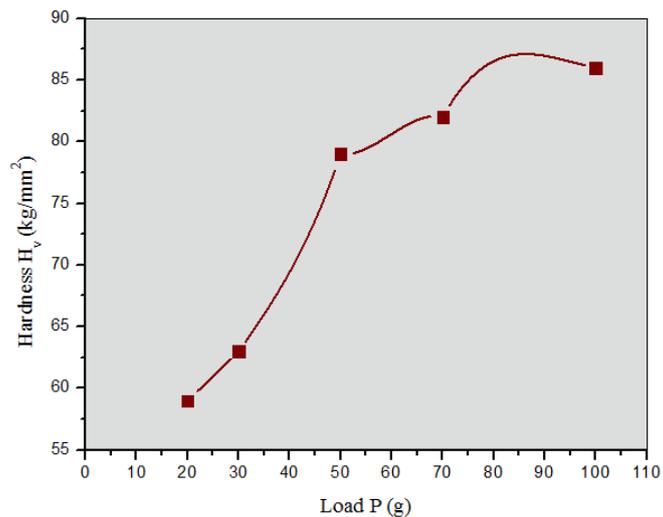


Fig. 7 : Variation of Hardness number with load