

Synthesis and Characterization of Nickel Urea Thiourea Single Crystal Developed by Slow Evaporation Method

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Abstract: A single crystal of nickel 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 studies showed the thermal properties of the crystals. The functional group of the grown crystals was identified by UV-Visible double beam spectra, FT-IR analysis, NMR and XRD studies.

Keywords: Urea, Thiourea, Nickel sulphate, Nickel urea thiourea single crystal, X-Ray diffraction

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 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 few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications¹⁻¹⁰. 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.

Experimental

0.78g of urea, 0.8g of thiourea and 1.08g of nickel sulphate 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 nickel sulphate 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 twenty days in order to get hard thiourea and urea doped single crystal.

Single crystals of nickel urea thiourea are grown by slow evaporation of the saturated aqueous solution at room temperature. Good qualities of single crystals were grown within twenty days. The photograph of the grown crystal is shown in Figure 1.



Figure 1. Photograph of the (NiTU) single crystal

NLO Studies

Kurtz second harmonic generation (SHG) test was performed to find the NLO property of the NiTU 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.

Results and Discussion

X-Ray Diffraction analysis

Single crystal X-ray diffraction study was performed for the grown NiTU crystal. It was found that NiTU crystal belongs to orthorhombic system ($\alpha = \beta = \gamma = 90^\circ$). Lattice parameter values of NiTU are compared with reported TU 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 NiTU crystal does not change the crystal system though there is a small change in the lattice parameters. The powder sample of NiTU 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 2). The Lattice parameter (a) was calculated by selecting the (102) plane using the formula².

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

Fourier transforms infrared spectroscopy

The FT-IR spectra of nickel urea thiourea grown crystals are shown in Figure 3. In the higher wavelength region, the peak at 3470 cm⁻¹ is assigned to C-H, N-H stretching vibration. The region 3450 cm⁻¹ and 3150 cm⁻¹ with strong intensity represents N-H stretching mode. The broad envelope positioned in between 3450 cm⁻¹ and 2615 cm⁻¹ corresponds to the symmetric and asymmetric stretching modes of NH₂ group. The peak at 2970-2910 cm⁻¹ with medium intensity refers C-H asymmetric stretching. Combinational overtones extend to the bands from 2300 -2250 cm⁻¹. The peak at 1730 cm⁻¹ indicating the C=O stretching mode of vibration.

The NH_2 bending vibrations occur at 1608 , 1593 and 820 cm^{-1} . The peak at 1540 cm^{-1} is due to NH_2 bending vibration. The peaks at 1440 - 1390 cm^{-1} corresponds to the $\text{C}=\text{S}$ stretching. The $\text{C}-\text{C}$ stretching mode of vibration occurs in 1330 cm^{-1} peak. The peak at 1205 cm^{-1} gives rise to $\text{C}-\text{N}$ stretching mode of vibration. The spectra show absorption bands in the region of 1090 cm^{-1} and 1045 cm^{-1} which are due to in-plane $\text{C}-\text{H}$ bending vibration. The band 1080 cm^{-1} signifies the $\text{N}-\text{H}$ symmetric bending. The bands at 830 cm^{-1} and 795 cm^{-1} revealed that $\text{C}-\text{N}$ deformation mode. The ring deformation occurs at 815 cm^{-1} . $\text{C}=\text{O}$ deformation is identified by the band at 678 cm^{-1} . $\text{C}-\text{H}$ out-of plane bending peaks obtained at 660 cm^{-1} and 648 cm^{-1} . The bands 668 - 632 cm^{-1} represents $\text{C}-\text{C}$ deformation. The absorption bands in the region of 476 - 463 cm^{-1} are due to $\text{N}-\text{C}$ stretching vibration. The assignments confirm the presence of various functional groups present in the material. The absorption around 1600 cm^{-1} is NH_2 bending and this band would be shifted into lower wavelength region 1618 cm^{-1} . Our investigations are well compared with earlier reports¹⁰⁻¹⁹.

Table 1. Lattice parameter values of NiTU and reported TU crystals

Sample	System	$2\theta(\text{degree})$	FWHM	hkl	Lattice parameter (\AA)	
					Calculated	Reference[2]
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
NiTU	Orthorhombic	28.4935	0.893	200	3.8300	3.9650
		19.7727	0.448	020	4.4864	4.5002
		20.6897	0.5033	002	4.2896	4.2999

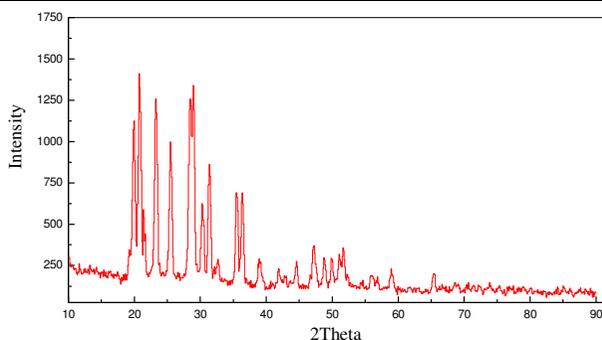


Figure 2. XRD pattern of the NiTU single crystal

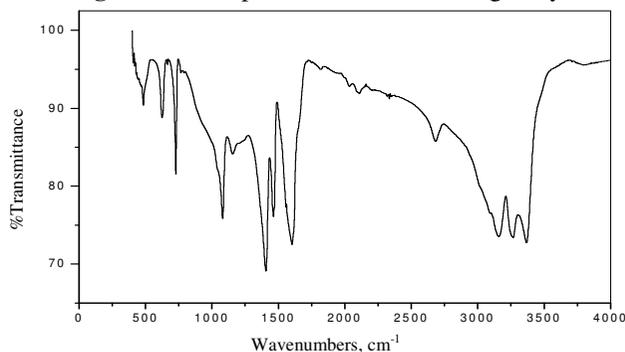


Figure 3. FT-IR spectrum of the NiTU single crystal

UV- Visible studies

The UV-Visible spectrum of the single crystal NiTU shown in Table 2 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 NiTU single crystal were found to be 279.2 nm, 311.5 nm, 340.9 nm and 480.8 nm respectively. The above values indicates the presence chromophores such as amino, imino, carbonyl and thio carbonyl groups and 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 3.87eV for pure and nickel 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 generation¹⁵⁻²⁷.

Table 2. UV-Visible spectrum data of NiTU Crystal

Crystal	Wavelength (nm)	% Transmittance
NiTU	279.2	68.5
	311.5	63.1
	340.9	87.9
	480.8	91.2

Nuclear magnetic resonance spectroscopy

NMR spectrum of NiTU was recorded using FT-NMR spectrometer. NiTU crystal was powdered and dissolved in deuterated dimethyl sulfoxide (DMSO). NMR spectrum recorded for NiTU is shown in Figure 4. A chemical shift at 7.708-7.831ppm is due to =C-NH-C= proton. The chemical shift at 7.371-7.458 ppm is assigned to O-C=O and N-H proton. Chemical shift at 9.280-9.714 ppm is due to -N-C=O. A chemical shift at 1.16 ppm is due to =C- proton¹². The chemical shift at 7.269-7.306 is due to H-N-C=O. A chemical shift at 3.528 is due to -C=S. The above values confirm the structure of NiTU.

Thermal analysis

TGA analysis of the NiTU crystal was carried out in the temperature range 10- 900 °C. The recorded thermogram is shown in Figure 5. From TGA curve it is observed that the weight loss start from 300 °C. 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 trace²¹.

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 relation²¹,

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

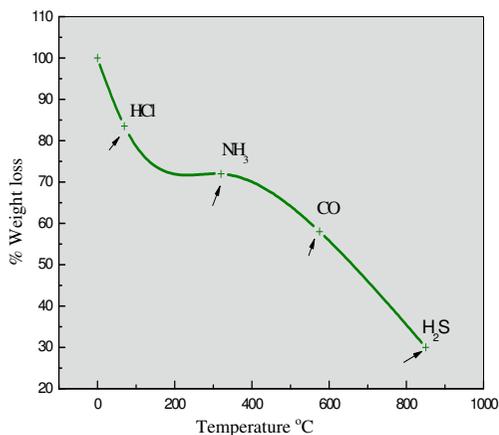


Figure 5. Thermogravimetric analysis for the determining the weight loss

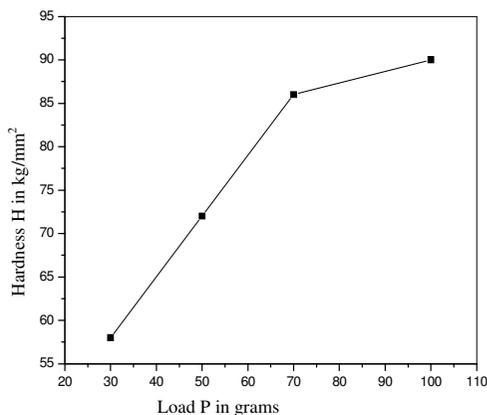


Figure 6. Variation hardness number with Load

Conclusion

The good quality single crystals of nickelurea 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 thermogram 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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