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Crystal growth and characterization of semiorganic material–Thiourea barium (zinc) chloride (TBZC)

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Semiorganic crystals of Thiourea barium (zinc) chloride (TBZC) were successfully grown by slow evaporation technique at room temperature. Studies on structural, optical properties of the crystal were carried out. Elemental analysis was confirmed the stoichiometric ratio. Powder X-ray diffraction (PXRD) analysis confirms the crystalline nature and purity. FT-IR spectrum confirms the presence of vibration molecules. Optical transmittance property was carried out by using UV-Visible spectrometer. Dielectric constant was measured for various frequencies as a function of temperature. Microhardness test has been measured the hardness of crystal.

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Keywords: Crystal growth from solution, CHNS analysis, Fourier transform infrared spectrum, Dielectric constant

1. Introduction

The nonlinear optical (NLO) materials have attracted great interest in the field of laser technology, optical communication and optical storage technology. The material requires NLO effect with thermal and mechanical stability for many device applications. The semi-organic materials having optical nonlinearity and the chemical flexibility of organics with the physical ruggedness of inorganics [1,2]. The metal-organic coordination complex of organic ligand is usually more dominant in the NLO field and dielectric effects [3]. In this connection, Metal complexes of thiourea include advantages of both organic and inorganic part of the complex and it has large dipole moment able to form the hydrogen bonds. The centrosymmetric thiourea molecule, when combined with inorganic salts yields non-centrosymmetric complexes which has nonlinear optical properties [4,5]. Thiourea zinc chloride has been already reported by Rajasekaran et al. and Sweta Moitra et al. [6,7]. In the present paper, barium chloride was added with thiourea zinc chloride and the crystal was grown from its aqueous solution by slow evaporation method. The grown crystals were characterized by CHNS, powder XRD, FT-IR, optical transmission, dielectric and microhardness study.

2. Experimental

2.1. Crystal growth

Thiourea barium (zinc) chloride (TBZC) crystal was synthesized by stoichiometric incorporation of thiourea, barium chloride and zinc chloride in the ratio of 1:1:1 and chemical equ. (1) is:

$$[CS\,(NH_2)_2] + BaCl_2 + ZnCl_2 \rightarrow Ba[CS\,[(NH_2)_2].Zn.Cl_4] \quad (1)$$

(Thiourea barium (zinc) chloride)

In order to achieve the crystal, first required amount of thiourea dissolved in double distilled water. Then the correct ratio of zinc chloride and barium chloride was dissolved separately. The solution was mixed and continuously stirring by using a magnetic stirrer until to form a clear homogenous solution. This process was continued for eight hours and finally the solution was kept in a glass vessel for crystallization. After 24 days, quality crystals were obtained and shown in Fig. 1.

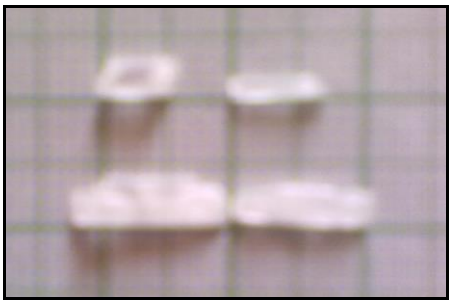

Fig. 1. As grown crystals of TBZC.

3. Results and discussion

3.1. CHNS analysis

The percentage compositions of the constituent elements present in TBZC crystals were determined by Elementar Vario EL III instrument. The percentages of carbon, hydrogen, nitrogen and sulfur are presented in Table-1. The experimental values are close to the calculated values and confirmed the stoichiometric ratio.

Table 1. Elemental analysis of TBZC crystal.

Sl.No.	Element	Experimental (%)	Calculated (%)
1.	C	3.06	2.86
2.	H	1.37	0.96
3.	N	6.01	6.66
4.	S	7.02	7.62

3.2. Powder X-ray diffraction

The powder from the TBZC was subjected to PXRD Analysis by using Rich-Seifert X-ray diffractometer Model Bruker AXS D8 Advance CuKα, Wavelength (1.5406 Å). All the observed prominent peaks are depicted in Fig. 2. The bragg's diffraction peaks were indexed hkl value and observed high intensity peaks confirm the crystalline nature and purity of grown crystal.

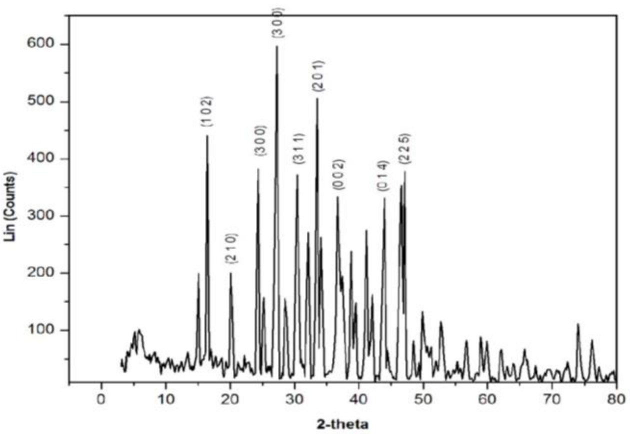

Fig. 2. Powder XRD pattern of TBZC crystal.

3.3. FT-IR analysis

The Fourier transform infrared spectrum was recorded by the KBr pellet technique using Thermo Nicolet, Avatar 370 Spectrometer to confirm the vibrational structure of the crystalline compound with range of wave number 4000-400 cm^{-1}, which is shown in Fig. 3. Sharp peaks observed at 3433 and 3109 cm^{-1} due to asymmetric and symmetric stretching of NH vibration of thiourea [8]. Peaks at 3314, 1621 and 1614 cm^{-1} correspond to the NH_2 deformation. The N–C–N vibration gives a peak at 1493 cm^{-1}. The symmetric N-C-N stretching ascribed at 1099 cm^{-1}. The small peaks at 1396 and 715 cm^{-1} due to the presence of C=S stretching. S-C-N- stretching is assigned at 476 cm^{-1} [6,9]. From the FTIR spectum, the observed wave numbers obtained from the TBZC crystal were found to be in good agreement with the assignments proposed in thiourea [10] reported in literature and are listed in Table 2.

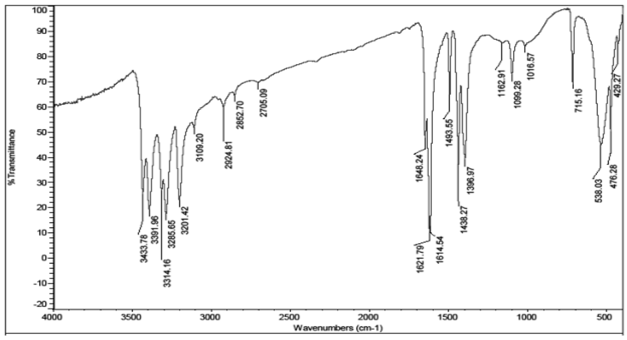

Fig. 3. FT-IR spectrum of TBZC crystal.

Table 2. FTIR spectral band assignments of TBZC crystal.

Wave number (cm^{-1})			Assignments
Thiourea [10]	ZTC [6]	TBZC	
3376	-	3391	NH_2 symmetric stretch
3280	-	3285	NH_2 symmetric stretch
-	2750	2852	NH_3^+ asymmetric stretch
1625	1612	1621	NH_2 bending
1470	1494	1493	N–C–N stretching
1417	1404	1396	C=S stretching
1083	1103	1099	N–C–N stretching
730	713	715	C=S stretching
494	-	476	S–C–N symmetric stretching

3.4. UV-Visible spectrum

The optical behavior of the crystal was assessed by using Perkin Elmer (Lambda 35) UV-Vis Spectrometer in the range of 150–1100 nm. An optical transmission spectrum is shown in Fig. 4. The crystal has lower cutoff wavelength occurs at 309 nm and the remarkable transmittance in the entire visible region of the spectra [11]. This is an advantage of the use of thiourea compound, where the absence of strongly conjugated bonds leads to wide transparency ranges in the visible and UV spectral regions.

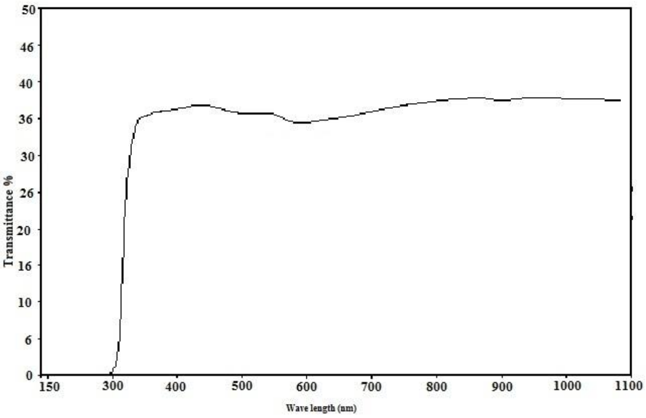

Fig. 4. UV-Visible Spectrum of TBZC crystal.

3.5. Dielectric constant

The dielectric property of TBZC was studied at various temperatures using Agilent A 2484. The dielectric constant (ε_r) of crystal was found by measuring the capacitance and dielectric loss, which is used to calculate the dielectric constant at various temperatures ranging between 30 to 150 ºC for five different frequencies namely (100Hz, 1KHz, 10KHz, 100KHz and 1MHz). From Fig. 5, the dielectric constant increased with increased the temperature [12]. The present study showed that dielectric constant was observed maximum at 150 ºC, since all types of polarization such as electronic, ionic, orientation and space charge polarizations occur at higher temperature.

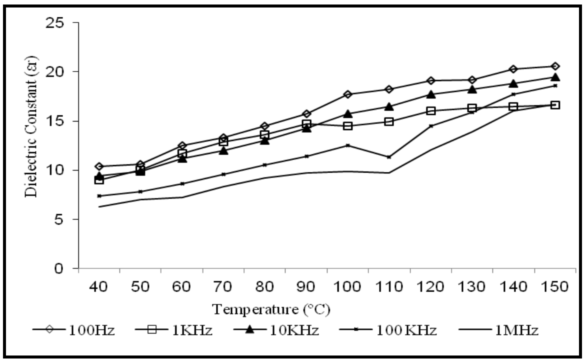

Fig. 5. Dielectric Constant of TBZC crystal.

3.6. Microhardness

Microhardness measurement is commonly used to determine the mechanical strength of the material which is related to bond strength and defect structure [13]. The static indentations were made on the surface of crystal by varying the load from 25-100g at room temperature. Vicker's microhardness number was determined using Hv=1.8544 P/d^2 (kg/mm^2). The variation of Hv with the applied load P is shown in Fig. 6. In our case, Hv increases with load up to 100g and which can be attributed to the work hardening of the surface and the maximum value of hardness for TBZC crystal at room temperature was found to be 53.4 kg/mm^2 for the load of 100g.

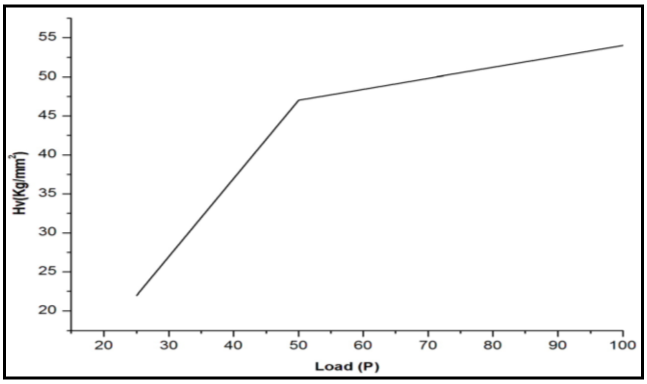

Fig. 6. Microhardness of TBZC crystal.

4. Conclusions

Good optical quality crystal of TBZC has been grown successfully by slow evaporation technique. The elemental analysis confirmed the stoichiometric ratio. The X-ray diffraction study confirms the crystalline nature and purity of the TBZC crystals. The presences of functional groups are identified by FT-IR spectrum. The optical properties of the grown crystal were evaluated from the transmission spectrum. From the microhardness study of the grown crystal has minimum surface hardness about 53.4 kg/mm^2. The variation of dielectric constant was studied with different frequency with function of temperature.

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