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Growth and dielectric study of ZTC semi organic nonlinear optical (NLO) crystal for electro-optic modulation

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Zinc thiourea chloride (ZTC), a semi organic non linear optical (NLO) crystal has been grown by slow evaporation technique at room temperature. The growth of ZTC crystal was confirmed by powder X-ray diffraction and the presence of different functional groups in grown ZTC crystal were confirmed by FTIR analysis. The UV-visible spectral studies were carried out in the range 200 nm to 800 nm. The lower cut off wave length lies below 300 nm. The large transmission in the entire visible region enables it to be good candidate for optoelectronics applications. The surface analysis of grown crystal was carried out by scanning electron microscopy (SEM). The thermal behavior has been studied by thermogravimetric analysis. The dielectric study was carried out by transmission line wave-guide method at two different frequencies as 8 GHz and 12 GHz. The dielectric studies revealed that as frequency increases dielectric constant (ε) decreases.

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1. Introduction

Electro-optic effect is one of the most technologically important applications of nonlinear optics being researched today [1-7]. The electro-optic effect affords the use of a DC electric field to alter the index of refraction of a material, allowing the fabrication of various types of optical modulator and switches for fiber-optics networks and communication.

Nonlinear optical (NLO) materials capable of generating the second harmonic frequency play an important role in the domain of optoelectronics and photonics. Nonlinear optical (NLO) material crystals have wide application in field of telecommunication, optical computing and optical data storage. In the last decade there has been tremendous progress in the development of the NLO materials having large nonlinear optical coefficients [8-12]. The organic and inorganic NLO crystals have some discrepancies in their structural, mechanical and thermal properties. The search for new frequency conversion material over the past decade has led to discovery of many semi-organic materials. These materials possess large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness. Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications [13-14].

Most of the researchers have reported growth mechanism and conventional characterization of ZTC crystal so for [15-17]. However, in the present communication in addition to conventional characterizations we have characterized grown ZTC crystal for measurement of dielectric constant using transmission line wave guide method at microwave frequency. This information will be more useful for fabrication of optoelectronic devices.

2. Experimental

2.1 Synthesis and growth

Initially the ZTC salt was synthesized by dissolving 1:2 ratio of GR grade of Zinc chloride and thiourea in de-ionized water of appropriate proportion. The solution was stirred with magnetic stirrer up to four hours at room temperature. After a period of one weak, we got a salt at the bottom of beaker. In order to obtain the more purity of salt, this was subjected to re-crystallization process. The required quantity of Zinc chloride and thiourea was estimated from following reaction.

$$ZnCl_2 + 2[CS\ (NH_2)_2] = Zn\ [CS\ (NH_2)_2]_2Cl_2 \qquad (1)$$

The calculated amount of salt was dissolved in the de-ionized water by constant stirring up to four hours, and the super saturation stage was achieved. The seed of ZTC crystal which was obtained earlier was suspended in this solution with the help of nylon thread. The pH of solution was 4.3. After three week duration a well-defined, transparent colourless ZTC crystal of size (19 mm x 8 mm x 4 mm) was harvested. The photograph of grown crystal is shown in Fig. 1.

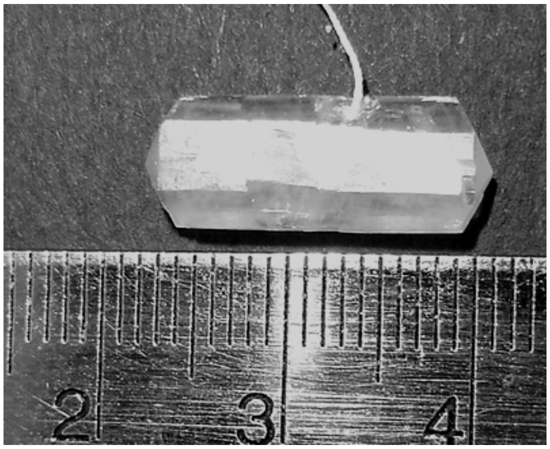


Fig. 1. Photograph of grown ZTC crystal.

2.2 Characterization

The grown crystal was characterized by powder XRD, Fourier Transform Infrared Spectroscopy (FTIR), UV-visible spectral analysis, Scanning Electron Microscopy (SEM), Thermogravimetric analysis, dielectric constant determination by transmission line wave-guide method.

3. Results and discussion

3.1 Powder X-ray diffraction

The crystalline structure of grown ZTC crystal was determined by Powder X-ray diffraction technique by 2nd differential method. The cell calculated parameters show very good resemblance with those earlier reported [13]. The X-ray diffraction pattern is shown in Fig. 2.

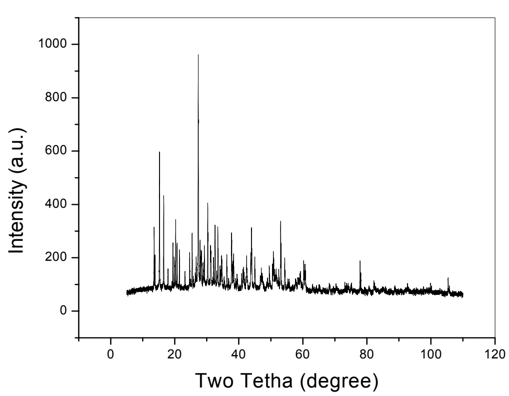


Fig. 2. Powder XRD pattern.

3.2 Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra of grown crystal is shown in Figure 3. There are two possibilities regarding co-ordination of Zinc with thiourea. The co-ordination of Zinc will takes place either with nitrogen or with sulphure of thiourea[16]. The formation of Zn-S bond expected to increase polar character structure of thiourea molecule. The high frequency NH absorption bands in region of 2700-3400 cm^{-1} for the thiourea spectrum were not shifted to lower frequencies on the formation of ZTC compound indicating that nitrogen to zinc bonds are not present and the bonding is in between sulphure and zinc atom. The study of spectra shows a shift in the frequency band in lower frequency region. The broad envelop in-between 3000-3444 cm^{-1} corresponds to symmetric and asymmetric stretching of NH_2 grouping of thiourea. It is also clear from the spectrum that symmetric and asymmetric C=S stretching vibrations are at 717-1417cm^{-1}. Similarly, C-N stretching vibration observed at 1105cm^{-1}, which is higher than thiourea (1089 cm^{-1}). This shows that binding of zinc with thiourea is through sulphure.

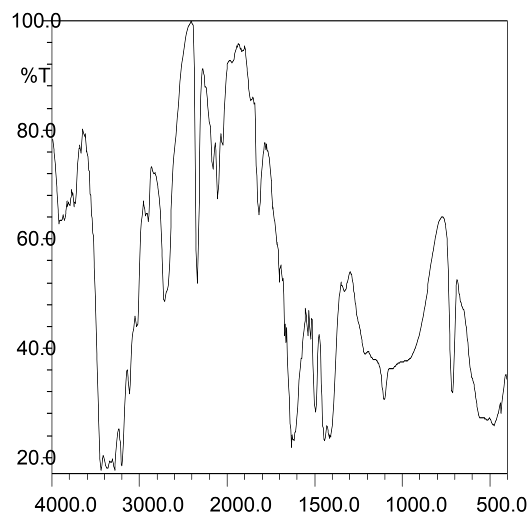


Fig. 3. FTIR spectrum of ZTC crystal.

3.3 UV-Visible spectral study

In order to find the range and percentage of optical transmission the UV-visible spectral study was carried out using Shimadzu 1601 UV-Vis spectrophotometer in the range of 200-800 nm and it is shown in Figure 4. The ZTC has a good transmittance and the lower cut off wavelength is just below 300 nm. The useful transmission range in the full visible region indicates that the material is a promising nonlinear optical material for optoelectronics applications.

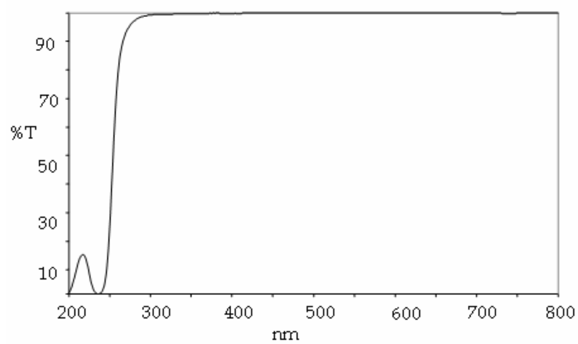


Fig. 4. UV-Vis transmittance spectra ZTC crystal.

3.4 Scanning Electron Microscopy (SEM)

The SEM study of grown ZTC crystal was carried out by using JEOL-JSM- 6360A Analytical Scanning Electron Microscope. The surface of grown crystal is almost flat with some growth hillocks. The SEM picture on a ZTC crystal is shown in Fig. 5.

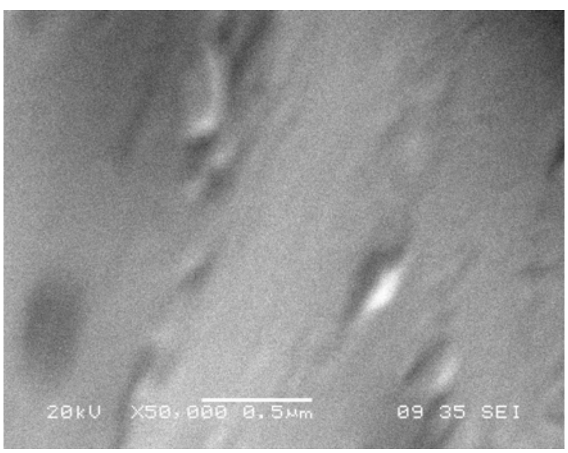


Fig. 5. SEM picture of surface of grown ZTC crystal.

3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis of grown ZTC crystal was carried out using TAQ-500 thermogravimetric analyzer between temperature limit 25°C to 800°C in heating rate of 25°C/min in a nitrogen inert atmosphere. The resulting thermogram and DTG trace are shown in Figure 6. The first weight loss is occurs at a temperature of 245.94°C. This is due to the removal of hydrogen from the thiourea molecule. The second weight loss is seen at the temperature of 302.23°C, it may be removal of carbon atom of thiourea molecule. The peak at the temperature of 387.18°C is attributed to the removal of sulphure from the zinc co-ordination. The thermogram shows that there is no free un co-ordinated thiourea in the sample because the melting point is 182°C, the decomposition starts at the 245.94°C and hence grown ZTC is thermodynamically stable up to the 245°C.

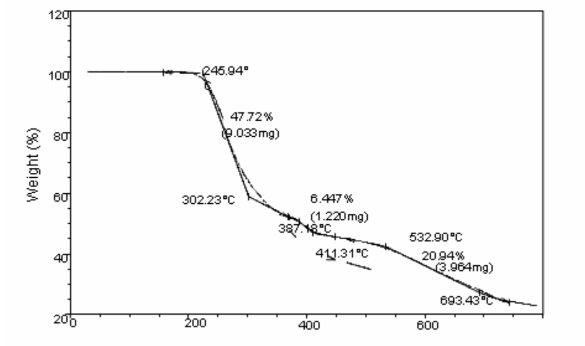


Fig. 6. TGA thermogram ZTC crystal.

3.6 Dielectric constant

The dielectric constant of grown ZTC crystal was determined using transmission line wave guide method in X-band and at frequency 8 GHz and 12 GHz at temperature 34ºC for different lengths of sample. First the standing wave pattern was obtained without keeping sample in wave-guide and then sample of ZTC was kept at different lengths. The relationship between distance and power was plotted and the wavelength "λg" was determine and then dielectric constant (ε) was calculated using following relationship.

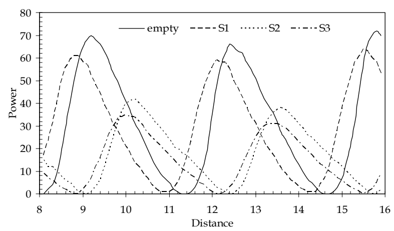
$$\varepsilon_r = \frac{(a^2/\pi^2)\,.(\beta l_\varepsilon/l_\varepsilon)^2 + 1}{(2a/\lambda g)^2 + 1}$$

Where a – area of wave guide

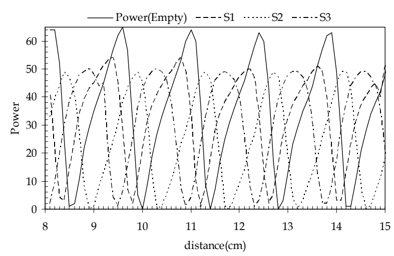
$$\beta - 2\pi/\lambda g$$

It was observed that as frequency increases the dielectric constant (ε) decreases. The results are shown in Table 1.

The crystals with high dielectric constant lead to power dissipation. The material having low dielectric constant will have less number of dipoles per unit volume. As a result it will have minimum losses as compared to the material having high dielectric constant [18-19]. Therefore low dielectric constant of grown crystal at higher frequency is an added advantage for high speed electro-optic modulation. The standing wave pattern with and without sample of different lengths, in the wave guide are shown in Fig. 7(a) and (b).



(a)



(b)

Fig. 7. (a) Standing wave pattern with and without sample for frequency 8 GHZ; (b): Standing wave pattern with and without sample for frequency 12 GHZ.

Table 1. The dielectric constants of ZTC crystal.

Frequency (GHZ)	Dielectric constant (ε)
8	12
12	5.56

4. Conclusions

The semiorganic nonlinear optical material crystal (ZTC) has been grown by slow evaporation technique at room temperature. The powder X-ray diffraction confirmed crystal structure while FTIR analysis gives assignment of different functional group. It is also evident from FTIR studies that binding of thiourea with zinc chloride occur through sulphure instead of nitrogen. The good optical transmittance in entire visible region makes the grown crystal a potential candidate for NLO applications. The thermogravimetric analysis (TGA) shows that ZTC crystal is thermodynamically stable up to 245°C. The dielectric measurements show that the dielectric constant decreases with increase in frequency. Low dielectric constant at higher frequency of ZTC crystal enables it to be good candidate for high electro-optic modulation.

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