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Studies on the optical and dielectric properties of a zinc thiourea chloride NLO single crystal

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ABSTRACT

Single crystals of a nonlinear optical material, zinc thiourea chloride were grown by the slow evaporation technique. The crystal structure and lattice parameters of the grown crystal were determined by the single crystal X-ray diffraction studies. The single crystal XRD revealed that the material crystallized in a orthorhombic crystal system. Optical studies were carried out and it was found that the tendency of transmission observed from the specimen, with respect to the wavelength of light, is practically more suitable for opto-electronic applications. The optical band gap is found to be 4.30 eV. Optical constants such as the band gap, refractive index, reflectance, extinction coefficient and real (ε_r) and imaginary (ε_i) components of the dielectric constant and electric susceptibility were determined from the UV–vis–NIR spectrum. The dielectric constant and dielectric loss of zinc thiourea chloride were measured in the different frequency range from 50 Hz to 5 MHz at different temperatures. Further, electronic properties, such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal have been estimated.

1. Introduction

The invention of high intensity laser has opened up many innovative ways to explore the nature of matter and its interaction with light. Nonlinear Optics (NLO) is one of the most interesting research fields, that has revealed a host of optical phenomena, such as second and third harmonic generations (SHG and THG), sum and difference frequency generations (SFG and DFG), and optical parametric generation (OPG). The search for new materials with high optical nonlinearity is a potential area for both academic and industrial purposes. These materials have attracted the interest of many theoretical and experimental researchers. Nonlinear optical materials capable of generating the second harmonic frequency, play an important role in the domain of optoelectronics and photonics. Within the last decade, much progress has been made in the development of these NLO organic materials, having a large nonlinear optical coefficient. In the recent past, there have been extensive efforts to develop inorganic, organic and semi organic NLO crystals [1–4]. Nonlinear optical materials find a number of applications like frequency conversion, optical switching, light modulation and optical memory storage. Recent researches reveal that organic nonlinear optical materials are used for developing relatively low-power laser-driven nonlinear optical systems. They exhibit less optical response time but high second harmonic generation (SHG) efficiency, compared to that of inorganic materials [5,6]. In the present work, an optically transparent zinc thiourea chloride single crystal was obtained, by the slow evaporation technique and its structural, optical and electrical properties are analyzed in detail.

2. Experimental procedures

Zinc thiourea chloride was synthesized by dissolving zinc chloride and thiourea in the molar ratio (1:2) in an aqueous medium. Calculated amounts of reactants were thoroughly dissolved in double distilled water and stirred well, by using a magnetic stirrer to ensure homogeneous solution, which was then filtered and transferred to a Petri dish. The prepared solution was allowed to evaporate at room temperature. The growth was initiated due to the slow evaporation of the solvent. The quality of the crystal was improved by the recrystallized process. After a period of two weeks, a crystal of transparent, good quality was harvested.

3. Results and discussion

3.1. Single crystal XRD

The lattice parameters were found to be $a = 5.89$ Å, $b = 12.66$ Å, $C = 12.91$ Å, $\alpha = \beta = \gamma = 90^\circ$ with unit cell volume $V = 962.99$ Å^3. From the data, it is observed that the grown crystal belongs to the orthorhombic system.

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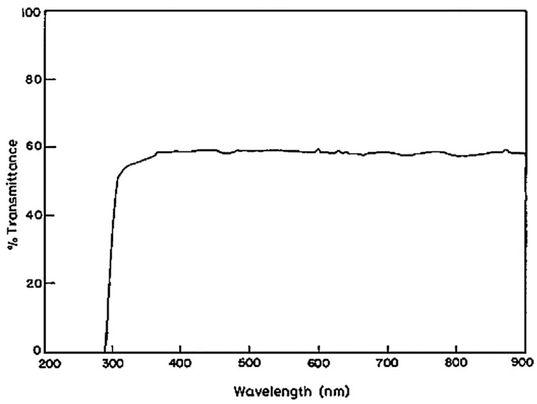

Fig. 1. UV–vis–NIR transmission spectrum of zinc thiourea chloride crystal.

3.2. Optical studies

The UV–vis–NIR absorption spectrophotometer was used to record the transmission spectrum in the range between 200 nm and 900 nm. From the observed spectrum (Fig. 1), the lower cut-off wavelength is found to be 290 nm. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the relation,

$$\alpha = \frac{2.3026\ \log(1/T)}{t} \tag{1}$$

where T is the transmittance and t is the thickness of the crystal. The optical bandgap (E_g) was evaluated from the absorption spectrum and optical absorption coefficient (α) near the absorption edge is given by,

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \tag{2}$$

where E_g is the optical band gap of the crystal and A is a constant. The Tauc's plot of $(\alpha h\nu)^2$ against the photon energy ($h\nu$) at room temperature (Fig. 2) shows a linear behaviour, (α-absorption coefficient and h-Planck's constant) which can be considered as an evidence of the indirect transition. Hence, assuming the indirect transition between valence band and conduction band, the bandgap (E_g) is estimated by the extrapolation of the linear portion of the curve to the point $(\alpha h\nu)^2 = 0$ [7]. Using this method, the band gap of the zinc thiourea chloride crystal was found to be 4.30 eV. As a consequence of wide the band gap, the grown crystal has a large transmittance in the visible region [8]. The extinction coefficient (K) can be obtained from the following equation:

$$K = \frac{\lambda\alpha}{4\pi} \tag{3}$$

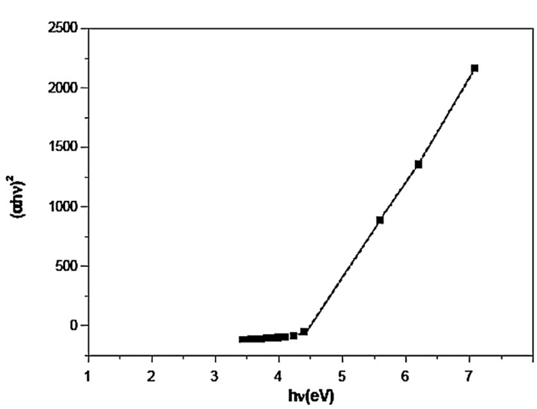

Fig. 2. Bandgap of zinc thiourea chloride crystal.

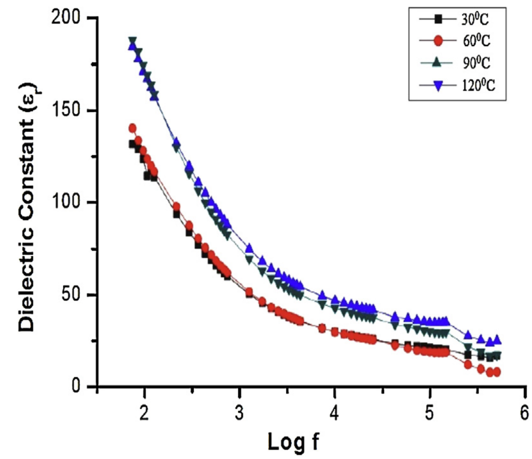

Fig. 3. Dielectric constant of zinc thiourea chloride, as a function of frequency.

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp\ (-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \tag{4}$$

Reflectance (R) in terms of the absorption coefficient, can be obtained from the above equation.

Hence,

$$R = 1 \pm \frac{\sqrt{1 - \exp\ (-\alpha t) + \exp\ (\alpha t)}}{1 - \exp(-\alpha t)} \tag{5}$$

The refractive index (n) can be determined from the reflectance data, using the following equation

$$n = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)} \tag{6}$$

The refractive index (n) is 1.58 at $\lambda = 900$ nm. From the optical constants, electric susceptibility (χ_C) can be calculated according to the following relation [9].

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{7}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{8}$$

where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The value of electric susceptibility χ_C is 0.171 at $\lambda = 900$ nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [10].

$$\varepsilon_r = n^2 - k^2 \quad \text{and} \quad \varepsilon_i = 2nk \tag{9}$$

The value of real ε_r and ε_i imaginary dielectric constants at $\lambda = 900$ nm are 1.323 and 7.253×10^{-5} respectively.

3.3. Dielectric properties

The dielectric constant and the dielectric loss of the zinc thiourea chloride were studied at different temperatures, using the HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. The dielectric constant was measured as a function of the frequency at different temperatures as shown in Fig. 3, while the corresponding dielectric losses are depicted in Fig. 4. The dielectric constant is evaluated using the relation,

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{10}$$