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Investigation on thiourea crystal grown in presence of ammonium acetate

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The optically good quality single crystals of thiourea crystal grown in presence of ammonium acetate have been grown by slow evaporation solution growth technique. The single crystal X-ray diffraction and FTIR have been studied for grown crystal. The UV-Vis transmittance spectrum has been recorded in the range of 200-900 nm. Theoretical calculations have been carried out to determine the linear optical constants such as extinction coefficient and refractive index. The analysis of third order non-linear optical properties like non-linear absorption coefficient (β), non-linear refractive index (n_2) and susceptibility (χ^3) have been calculated using Z-scan technique. The dielectric and mechanical strength of doped crystals have been investigated and results are discussed.

Keywords: Crystal growth, UV-Vis, Z- scan studies, Dielectric studies, Mechanical studies

1 Introduction

Single crystals with the enhanced optical, electrical, thermal, dielectric and mechanical properties have extensive application range in the field of frequency conversion devices. The NLO crystals were attracted by new researchers for technical applications in laser technology, communications and optoelectronics[1,2]. Thiourea is good organic material intensively used due to wide dipole moment and ability to form extensive network of hydrogen bond[3]. The inorganic materials form bonding with centrosymmetric thiourea molecules and forms noncentrosymmetric material which is prime requirement to satisfy second order non linearity of the material[4]. The well known organometallic complexes reported in the literature were tetrathiourea copper chloride, bisthiourea bismuth chloride, potassium thiourea chloride, zinc tris thiourea sulfate[5-8]. The organometallic complexes have advantageous features like good crystalline perfection, high nonlinearity, enhanced optical properties, lower dielectrics, high thermal stability and good mechanical strength[9]. The higher optical transparency, lower cut off and influential optical parameters of crystal were augmented characteristics for the fabrication of optoelectronic devices[10]. The result of third order nonlinear optical properties of various thiourea metal complexes shows its reliability for wide technological optical applications[11]. From the analysis of Z-scan technique it is observed that the thiourea crystal grown in presence of ammonium acetate shows superior magnitude of real and imaginary parts of third order nonlinear susceptibility and nonlinear refractive index. We are reporting first time synthesis and growth of thiourea crystal in presence of ammonium acetate by slow evaporation method at room temperature. The investigation has been accomplished by means of single crystal X-ray diffraction, Fourier transform infrared (FTIR), UV-Vis, second and third order nonlinear optical, hardness and dielectric study.

2 Synthesis

The thiourea crystal grown in presence of ammonium acetate was synthesized using AR grade ammonium acetate and thiourea in a molar ratio 1:2 by slow solvent evaporation solution growth technique at room temperature. The initial quantity of thiourea and ammonium acetate was taken as 91.34 g and 46.25 g, respectively. The deionized water is used as a solvent for synthesis and the molar solution of ammonium acetate and thiourea is well stirred for 6 h. Then the solution is filtered using Whatman filter paper and kept undisturbed for slow evaporation. The purity of the salt was improved by successive recrystallization using deionized water. The slow evaporation of aqueous solutions of thiourea crystal

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grown in presence of ammonium acetate was maintained at 40 °C in a constant temperature bath of accuracy ± 0.01 °C. The well phase, colorless and good transparent single crystals of thiourea crystal in presence of ammonium acetate were grown within two weeks as shown in Fig. 1.

3 Results and Discussion

3.1 Single crystal X-ray diffraction studies

The single crystal X-ray diffraction study of thiourea crystal grown in presence of ammonium acetate was carried out using Enraf Nonius CAD4-MV31 crystal X-ray diffractometer. From the single crystal XRD analysis, it is confirmed that the crystal belongs to the Orthorhombic P crystal system with centrosymmetric space group Pnma which confirms the absence of second order nonlinearity in the material[12]. The determined lattice parameter values are a = 5.53 Å, b = 7.71 Å, c = 8.65 Å, $\alpha = 90^0$, $\beta = 90^0$, $\gamma = 90^0$ and of volume 369 $(Å)^3$. Thiourea and acetate forms a layered structure. These layers are interlinked through H-bonding which results in tunnel like structure. At the centre there may be vacant space which may be occupied by ammonium ion[13,14].

3.2 Fourier transforms infrared (FTIR) spectral analysis

The FTIR spectrum of thiourea single crystal grown in presence of ammonium acetate has been recorded using Bruker α-ATR spectrophotometer in the range of 500 cm^{-1} to 4000 cm^{-1} is shown in Fig. 2. The assignments observed in the transmittance spectrum of grown crystal at 670 cm^{-1} correspondences to C-S stretching of the sulfur compound. The band observed at 1517 cm^{-1} is due to NH_4^+ ions and O-H stretching. The wave number peak at 1706 cm^{-1} is assigned due to C=O stretching. The peak at 2366 cm^{-1} and 3600 cm^{-1} in the spectrum can be assigned to C-H stretching and O-H stretching respectively[15].

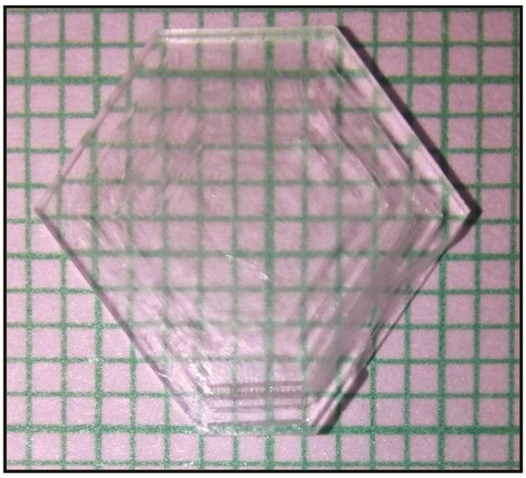

Fig.1 – Photograph of thiourea crystal grown in presence of ammonium acetate.

3.3 UV-visible transmission studies

The UV-visible of thiourea crystal grown in presence of ammonium acetate single crystal of thickness 1 mm was carried out using Shimadzu UV-2450 spectrophotometer in the range of 200-900 nm. The spectrum of transmittance as a function of wavelength was shown in Fig. 3(a) and the grown crystal is optically transparent up to 84% in the entire visible region. The sharp fall of transmittance curve ascertained as cut off wavelength and was observed at 295 nm for the grown crystal. The high optical transmittance of grown crystal might have been attributed to high optical homogeneity and minimum absorption and scattering from defect centers[16-18] (structural and crystalline). The high and wide

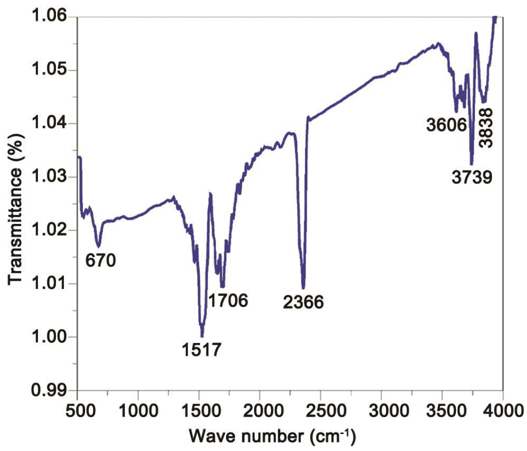

Fig. 2 – FTIR spectrum of grown crystal.

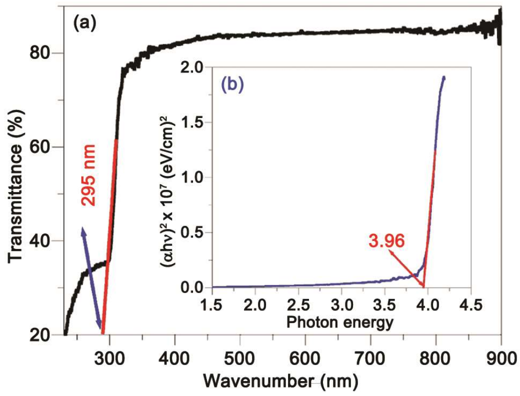

Fig. 3 – (a) Transmittance spectrum and (b) Tauc's plot .

transmittance in the UV- visible region with lower cut off wavelength shows its suitability for the different optical applications[19]. The optical absorption coefficient was calculated from the transmittance by using formula:

$$\alpha = \frac{1}{d}\mathrm{Ln}\frac{1}{T}, \qquad \text{... (1)}$$

Where T is the transmittance and d is the thickness of the crystal. The Tauc's plot justifies the dependence of absorption coefficient on the incident energy of photons by the relation:

$$\alpha h\nu = A(h\nu - Eg) \qquad \text{... (2)}$$

Where E_g is the optical band gap and A is constant. The interception of the linear vertical line in the Tauc's plot (Fig. 3(b)) on the photon energy axis is the value of E_g and was found to be 3.96 eV. The refractive index which is the propagation of light through medium of the material is depicted in Fig. 4(a). It is calculated by using formula:

$$n = [\tfrac{1}{T} + (\tfrac{1}{T} - 1)] \qquad \text{... (3)}$$

It is observed from Fig. 4(a) that, the refractive index value is 1.6 beyond wavelength 400 nm is saturated. Similarly, reflectance of grown crystal is evaluated by the relation:

$$R = (n-1)^2/(n+1)^2 \qquad \text{... (4)}$$

And, it is observed from the Fig. 4(b) that reflectance have saturated value 5.6% beyond wavelength[20] 450 nm. The high band gap energy value and lower magnitudes of reflectance and refractive index prove the suitability of grown crystal for antireflection coating in solar thermal devices[21]. The optical conductivity ($\sigma_{op} = \alpha nC/4\pi$), where, α is absorption coefficient, n is refractive index and C is the velocity of light. The Fig. 5(a) shows response of optical conductivity with photon energy. The optical conductivity of the grown material has higher values at higher photon energy indicate to increase in the absorption coefficient in this region[22]. The response of extinction coefficient as a function of wavelength is depicted in Fig. 5(b). The dielectric response of grown crystal is depicted in Fig. 6(a,b). The lower dielectric (real and imaginary) values and lower extinction value suggest grown crystal is suited for distinct integrated optical applications[23,24].

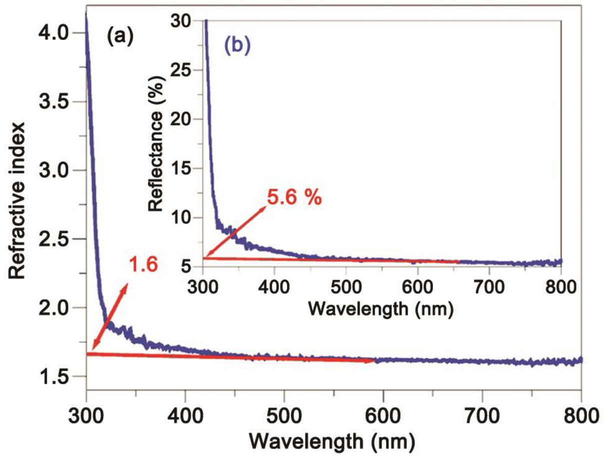

Fig. 4 – (a) *R.I* and (b) reflectance versus wavelength.

3.4 Z-scan studies

The Z-scan technique to determine the third order nonlinear optical properties of the crystal was introduced by Sheikh-Bahae *et al.*[25]. The optical resolution set up used for the Z-scan analysis is given in the Table 1. The well-polished thiourea crystal

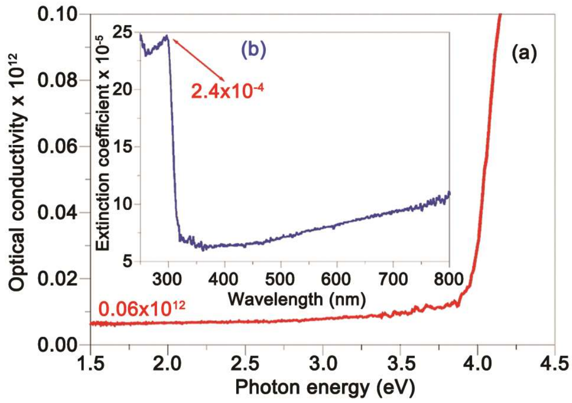

Fig. 5 – (a) Optical conductivity versus E and (b) extinction coefficient versus λ.

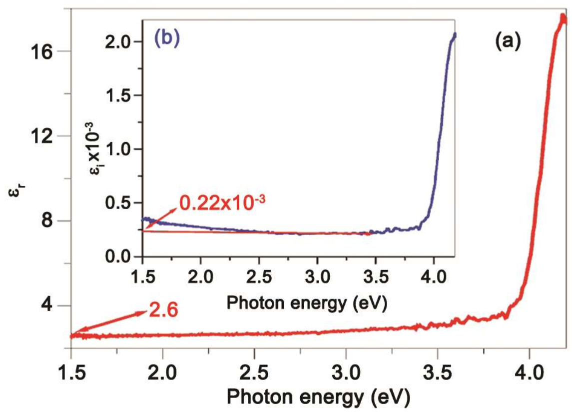

Fig. 6 – (a) ε_r versus photon energy and (b) ε_i versus photon energy.

grown in presence of ammonium acetate of thickness 0.65 mm is used for analysis of third order NLO property. The thickness of the crystal is important to minimize phase transition in Z-scan experiment. And the variations in transmittance intensity of the laser beam depend on the aperture size during the experiment. The He-Ne laser of wavelength 632.8 nm is focused on crystal through the focal lens of focal length 30 cm. The crystal is translated from -*Z* axis to +*Z* axis that is along the path of the laser beam and the intensity of the beam is measured at a far distance using a digital power meter. In closed aperture Z-scan configuration, the position of crystal sample was changed along *Z* direction and the transmittance was recorded through the closed slit of photo detector placed at a far distance. The nonlinear refractive nature of crystal causes self-focusing or self-defocusing effect[26,27]. The closed aperture z-scan response of thiourea crystal grown in presence of ammonium acetate was depicted in Fig. 7. It is observed that normalized transmittance peak followed by transmittance valley shows that the grown crystal have negative refractive index indicating self-defocusing nature. The materials refractive index and the absorption behaviour of the solid single crystal affect the intensity of the laser beam at the focal plane along the optical axis. The negative refractive index of grown crystal proves its prominence in optical night vision sensor devices[28].

Table 1 – Optical resolution of Z-scan setup

Parameter	Magnitude
Laser beam wavelength (λ)	632.8 nm
Lens focal length (*f*)	30 mm
Optical path distance (*z*)	85 cm
Beam waist radius (w_a)	3.3 mm
Aperture radius (r_a)	2 mm
Sample thickness (*L*)	0.5 mm
Intensity at focus (I_0)	26.50 MW/m^2

In the present study thiourea crystal grown in presence of ammonium acetate increases divergence by creating enhancement in the laser beam intensity at the focal plane and saturation absorption enhances the peak and the suppress valley at the focal point along optical axis. To study open aperture response, intensity dependent absorptions were collected directly from the detector by placing the lens in front of it. Figure 8 depicts the open aperture response of grown crystal and possesses reverse saturable absorption phenomenon[28].

From the closed aperture data (Fig. 7) the difference between peak and valley transmittance is evaluated with the help of equation:

$$T_{P-V} = 0.406(1-S)^{0.25}\,\Delta\phi \qquad \ldots (5)$$

Where *S* is the linear transmittance aperture derived by the equation:

$$S = [1-\exp(-2r_a^2/\omega_a^2)] \qquad \ldots (6)$$

Where r_a is the aperture radius and ω_a is the beam radius at the aperture. The magnitude of third order nonlinear refractive index for grown crystal using Z-scan data analysis is calculated by using formula:

$$n_2 = (\Delta\phi / K I_o L_{eff}) \qquad \ldots (7)$$

This includes *K* as a function of wave number determined by using wavelength as $K = (2\pi/\lambda)$, I_o is an intensity of laser beam at the focus *Z*=0 and L_{eff} is the effective thickness as a function of linear absorption coefficient (α) and thickness (*L*) of the sample given by $L_{eff} = [1-\exp(-\alpha L)]/\alpha$. The value of

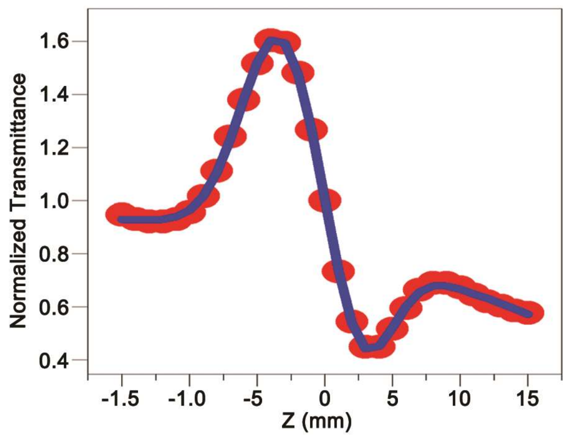

Fig. 7 – Close aperture.

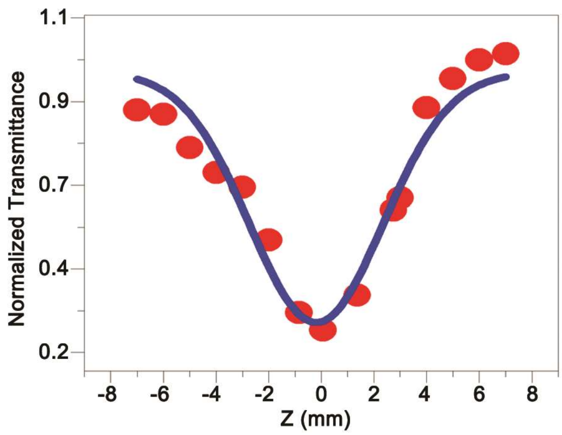

Fig. 8 – Open aperture.

the third order nonlinear refractive index of grown crystal is calculated as 3.07×10^{-7} m^2/W. From the open aperture Z-scan curve by means of one peak value (ΔT) as depicted in Fig. 8, the third order nonlinear absorption coefficient was evaluated by equation:

$$\beta = [(2\sqrt{2}\Delta T)/ I_o L_{eff}] \quad \ldots (8)$$

The value of nonlinear absorption (β) of grown crystal is found to be 1.12×10^{-8} m/W. The real and imaginary part of third order nonlinear susceptibility of grown was calculated as below:

$$\mathrm{Re}\,\chi^{(3)}(esu) = 10^{-4}(\varepsilon_0 C^2 n_0^{\ 2} n_2)/\pi \quad (cm^2/W)$$

$$\mathrm{Im}\,\chi^{(3)}(esu) = 10^{-2}(\varepsilon_0 C^2 n_0^{\ 2} \lambda\beta)/4\pi^2 \quad (cm/W) \quad \ldots (9)$$

Where, ε_0 is the permittivity of the vacuum, n_0 is the linear refractive index of grown crystal and C is the light velocity in vacuum. Thus, we can produce the resultant value of χ^3 by using equation:

$$\chi^3(esu) = \sqrt{(\mathrm{Re}\,\chi^3)^2 + (\mathrm{Im}\,\chi^3)^2} \quad \ldots (10)$$

The values of real and imaginary susceptibility of grown crystal were found to be 1.70×10^{-6} esu and 3.12×10^{-8} esu, respectively. The calculated value of the third order nonlinear susceptibility (χ^3) of grown crystal has higher magnitude as 1.71×10^{-6} esu and it is due to the π-electron delocalization which makes the molecule highly polarized[21]. Table 2 shows the comparison of third order nonlinear refraction (n_2) and susceptibility (χ^3) of grown crystal and other thiourea metal complex crystals. Thus thiourea crystal grown in presence of ammonium acetate is promising third order non linear material and plays the vital role in the applications optical limiting and photonic devices[28,29].

3.5 Dielectric studies

The thiourea crystal grown in presence of ammonium acetate of 2 mm size is subjected to frequency dependent dielectric studies using Gwinstek-819 LCR meter in the range of 10 Hz to 100 KHz. The dielectric constant and dielectric loss response of grown single crystal with frequency is shown in Figs 9 and 10. The dielectric constant and dielectric loss were determined by using formula $\varepsilon = Cd/\varepsilon_o A$, where, C is the capacitance, d is the thickness and A is the area of crystal sample. Dielectric loss was calculated using the formula, Tan $\delta = \varepsilon/\varepsilon_0$. It is observed that the magnitude of dielectric constant and dielectric loss of grown crystal is higher at lower frequency region is contributed by electronic, ionic, dipolar and space charge polarization mechanism replies the fewer defects in crystal[30]. While, the lower saturated values of dielectric constant in high-frequency region indicate

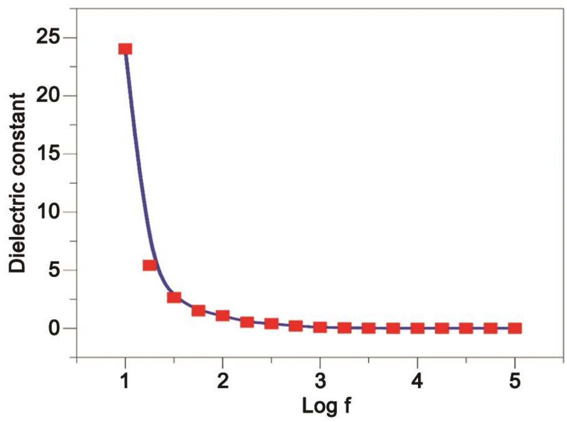

Fig. 9 – Dielectric constant versus Log *f*.

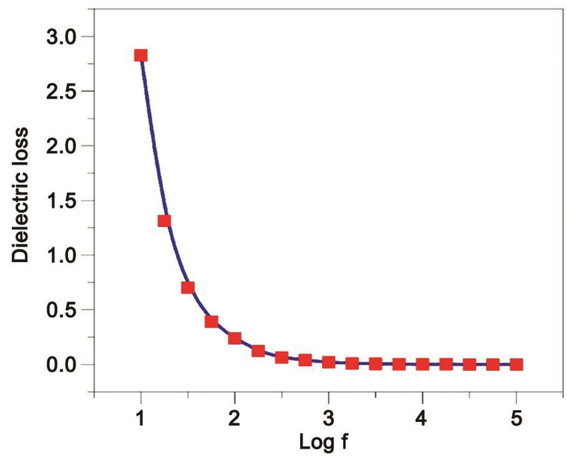

Fig. 10 – Dielectric loss versus Log *f*.

Table 2 – Comparison of third order nonlinear refraction and susceptibility.

Crystal	CBTC	BTZA	BTZB	BTZC	BTCF	Thiourea crystal in presence of AA
n_2 (esu)	-9.02×10^{-11}	-2.11×10^{-6}	-5.41×10^{-8}	-6.64×10^{-8}	-9×10^{-13}	-3.07×10^{-7}
χ^3(esu)	3.56×10^{-5}	1.67×10^{-6}	3.05×10^{-6}	3.6×10^{-6}	1.38×10^{-8}	1.71×10^{-6}
Reference	[11]	[11]	[11]	[11]	[11]	Present study

diminished polarization activity which favors fast molecular alignment of dipolar along the applied field. The response of low value of dielectric constant at high frequencies shows the prominence of the material in the field of optoelectronic and NLO devices[31].

3.6 Hardness studies

The Vickers hardness testing of thiourea crystal grown in presence of ammonium acetate was carried out using Shimadzu, HMV-2T microhardness tester. For each load P, an average of two impressions were recorded and the average of diagonal lengths (d in mm) of the indentation mark after unloading was measured using a calibrated micrometer attached to the eyepiece of the microscope. The hardness behavior of grown crystals was studied at different loads (25, 50 and 100 g) for constant indentation time 5 s. The Vickers microhardness value was calculated using formula, H_v=1.8544 (P/d^2) Kg/mm^2, where, p is the applied load (g) and d is the average diagonal length (mm) of the indentation mark[32]. The plot of Vicker's hardness (H_v) for grown crystal is shown in Fig. 11(a). The Meyer's law gives an expression regarding load and size of indentation, $p=k_1 \times d^n$, where, k_1 is the material constant and n is work hardening index. The graph is plotted between log p and log d, as shown in Fig. 11(b), and n value is found to be 6.0. According to Onitsch criterion, the calculated n value suggests that the grown crystal belongs to soft material[33]. The elastic stiffness coefficient was calculated using Wooster's empirical relation as $C_{11} = H_v^{7/4}$. The yield strength (σ_y) of the grown crystal was calculated by using formula $\sigma_y = (0.1)^{n-2} H_v/3$. The resistance to fracture indicates the toughness of a material and the fracture toughness K_c determines how much fracture stress is applied under uniform loading and is given by a relation[34] $K_c = P/ \beta_0 l^{3/2}$ for $l \geq d/2$. Where, β_0 is the indenter constant, equal to 7 for the Vickers's diamond pyramid indenter and the crack length (l) is the average of two crack lengths for each indentation. Brittleness is the property of the material which affects the mechanical behaviour of a material and is expressed in terms of the brittleness index (Bi) as Bi = H_v/K_c. The elastic stiffness coefficient (C_{11}), yield strength (σ_y), coefficient fracture toughness (K_c) and brittleness index (B_i) at 25 g, 50 g and 100 g for doped material were tabulated in Table 3. From the hardness parameters, the binding forces between the ions are quite strong and grown crystal is good engineering material and well suited for device fabrication[35,36].

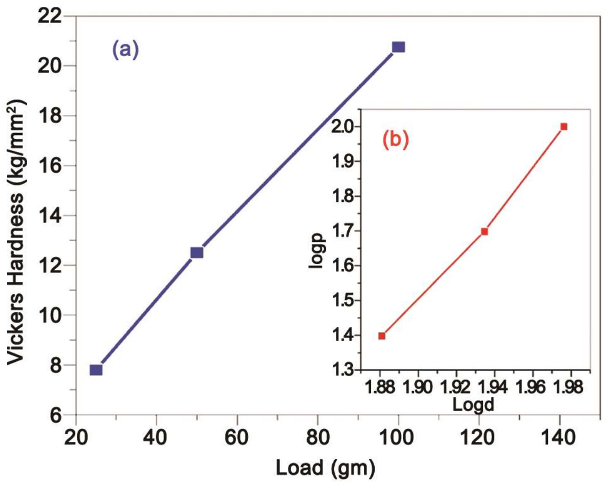

Fig. 11 – (a) Vickers hardness number versus load and (b) Log p versus Log d.

Table 3 – Elastic stiffness constants of grown crystal.

Load P (gm)	H_v (kg/mm^2)	σ_y (MPa)	$C_{11}\times10^{14}$ (Pa)	$K_c\times 10^4$ (kg m$^{-3/2}$)	$B_i \times10^3$ (m$^{-1/2}$)
25	7.8	4.041	0.625	1.051	7.274
50	12.5	6.476	1.428	2.103	5.828
100	20.75	10.75	3.466	4.206	4.837

4 Conclusions

The optically transparent thiourea crystal grown in presence of ammonium acetate was grown by slow evaporation technique at room temperature. The molecular structure has been confirmed by single crystal XRD and Fourier transform infra red (FTIR). The grown crystal has wide transparency in the entire UV-visible and improved optical parameters. The third order nonlinear susceptibility of grown crystal was found to be 1.71×10^{-6} esu, concludes the strong self-defocusing nature. The microhardness studies confirmed that the grown crystal belongs to the soft material category. The dielectric constant and dielectric loss have higher values at lower frequencies. The results suggest that grown crystal has applications in the technological photonic devices utilized in optical limiting systems, night vision sensors, optical switching and solar thermal devices.

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