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Linear and Third Order Non-Linear Optical Properties of Urea Salicylic Acid Crystal

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An organic non-linear optical crystal urea salicylic acid was grown by slow evaporation method using the mixed solvent of ethanol and water in equal ratio. The lattice parameters of urea salicylic acid crystal were obtained by single X-ray diffraction study. The optical transmittance study revealed the good transmission window of the urea-salicylic acid and its suitability for optical applications. The non-linear refractive index, n_2, absorption coefficient, β and third order susceptibility, $\chi^{(3)}$ have been measured through the Z-scan technique with He-Ne laser at 632.8 nm. The grown urea salicylic acid crystal exhibits two photon absorption and self-defocussing performance.

Keywords: Crystal growth, X-ray diffraction, Optical properties.

INTRODUCTION

Non-linear optical (NLO) is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching and optical memory for the emerging devices, in areas, such as telecommunications, signal processing and optical interconnections [1-4]. The urea molecule has two amide (—NH_2) groups joined by a carbonyl (C=O) functional group. It has shown interesting properties for non-linear optical applications [5]. Salicylic acid forms intermolecular hydrogen bonds exclusively to urea. The compound urea salicylic acid was formed from the strongly organic compound of urea and weak carboxylic acid of salicylic acid. The Z-scan technique is a popular and powerful method for the non-linear optical properties determination of semiconductors, dielectrics, organic or carbon-based molecules and liquid crystals because of its sensitivity, simplicity and ability to determinate the signs and magnitudes of optical non-linearity [6]. The Z-scan technique is based on the principles of spatial beam distortion and offers simplicity as well as high sensitivity for measuring both the non-linear refractive index and non-linear absorption coefficient [7-9]. This technique is based on the principles of spatial beam distortion. This method allows the simultaneous measurement of both non-linear refractive index (n_2) and non-linear absorption coefficient (β) of urea salicylic acid crystal. In the present work, the single crystal of urea salicylic acid was grown by slow evaporation method using the mixed solvent of water and ethanol. The grown urea salicylic acid crystal was subjected to single crystal X-ray diffraction study, ultraviolet-visible spectroscopy and Z-scan technique to confirm its structural, linear and non-linear optical properties.

EXPERIMENTAL

Synthesis and crystal growth: The urea salicylic acid salt was synthesized using high-purity urea and salicylic acid in equal molar ratio. The calculated amount of salts was dissolved in the mixed solvent of water and ethanol with equal molar ratio at room temperature. The solution was stirred well using a magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution. The saturated solution was filtered and crystallization was allowed to take place by slow evaporation method. Transparent and colourless crystals were harvested in a period of 15 days. The photograph of the grown crystals is shown in Fig. 1.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction study: The unit cell parameters and crystal structure of urea salicylic acid were determined from single crystal X-ray diffraction data obtained with a four-circle Nonius CAD4 MACH3 diffractometer (graphite mono chromated, MoK_α = 0.71073 Å) at room temperature (293 K). The urea salicylic acid crystal belongs to monoclinic structure of space group C2/c with unit cell dimensions, a = 22.825 Å, b = 5.1182 Å, c = 17.143 Å, β = 106.053°, V = 1879.1 $Å^3$ and Z = 8. The determined values of lattice parameters are very well agree with the reported values [10].

Fig. 1. As grown crystals of urea-salicylic acid

UV-visible-NIR transmittance study: The transparency of the crystal plays an important role in optical device fabrication and optical signal processing [11-13]. The UV-visible-NIR optical transmittance spectrum of urea salicylic acid crystal was recorded using Labindia 3032 UV-visible-NIR spectrophotometer with thickness of 2 mm in the range of 190-900 nm. The transmittance spectrum of the urea-salicylic acid is shown in Fig. 2(a). From the transmittance spectrum, It is clear that the grown crystal has good transmission in the entire range of between 347 nm and 900 nm. The cut off wavelength (λ_c) is found to be 347 nm. The calculated band gap value of the grown urea salicylic acid crystal is 3.58 eV. The absorption coefficient (α) and the optical constants, such as extinction coefficient (K), reflectance (R) and linear refractive index (n) are determined from the transmission (T) spectrum using the following relations,

$$\alpha = \frac{2.303 \log\left(\frac{1}{T}\right)}{t}$$

where, t = thickness of the crystal. The extinction coefficient (K) of grown urea salicylic acid crystal is calculated as:

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

where λ = wavelength of the radiation. The reflectance (R) in terms of absorption coefficient (α) can be obtained as

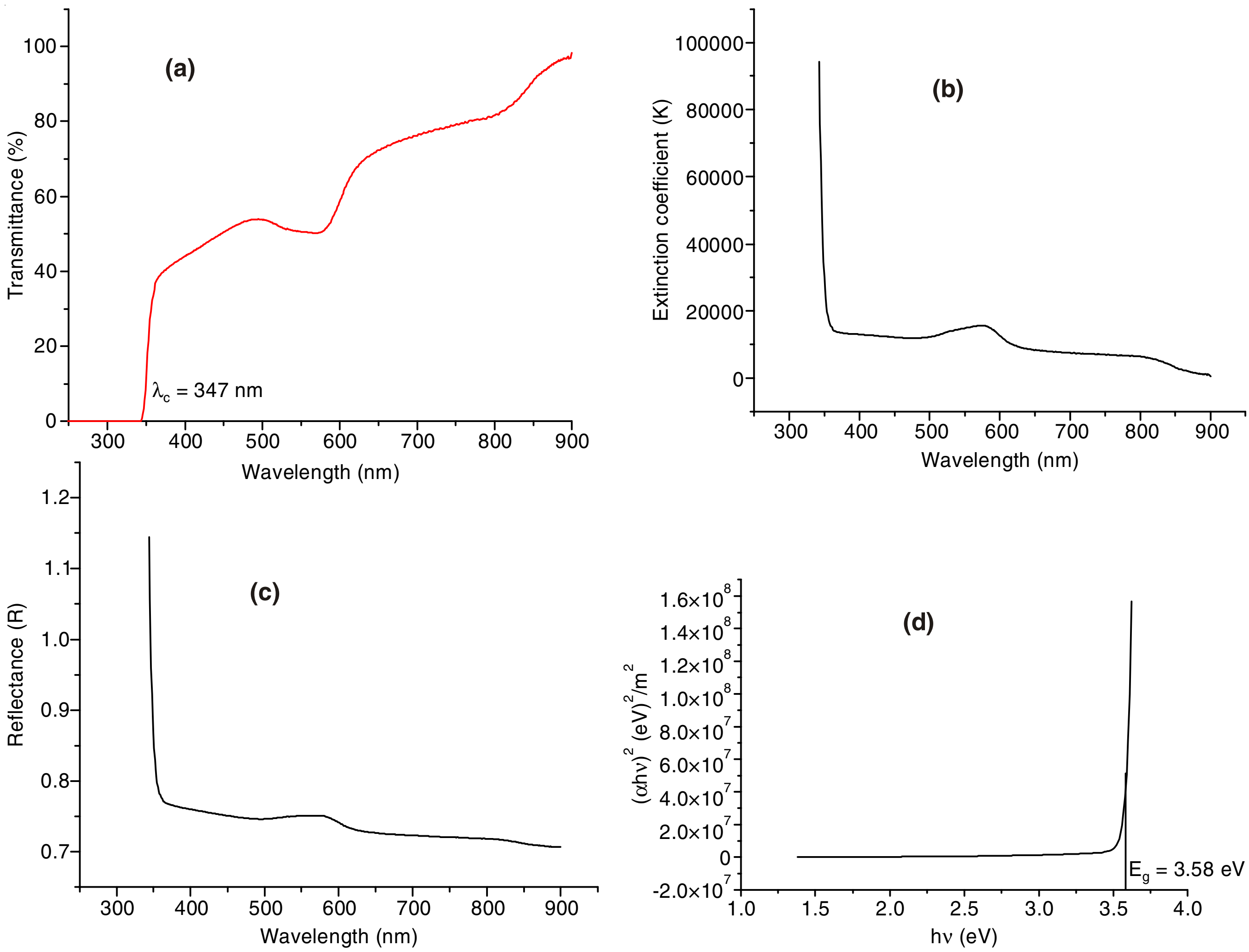

Fig. 2. (a) UV-visible-NIR transmittance spectrum, (b) Extinction coefficient *vs.* wavelength, (c) Reflectance *vs.* wavelength and (d) Tauc's plot of urea salicylic acid crystal

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

Fig. 2(b) and 2(c) illustrate the dependence of extinction coefficient (K) and reflectance (R) on the wavelength. Refractive index (n) can be determined from reflectance data using the following equation,

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

The linear refractive index (n) is calculated as 1.45 at the cut off wavelength (λ_c = 347 nm). Fig. 2(d) shows the Tauc's plot [hν *versus* $(\alpha h\nu)^2$] of the urea salicylic acid crystal, where α = absorption coefficient and hν = photon energy. The band gap energy as determined from the Tauc's plot is found to be 3.583 eV which is matched with the observed value of band gap from transmission spectrum. This indicates that urea salicylic acid is a higher band-gap energy material. The less absorbance in the visible region makes the urea salicylic acid crystal a good optical window material [14].

Refractive index analysis: The refractive index of urea salicylic acid single crystal was measured using Abbe's refractometer model (ATAGO, NAR-4T, Japan) connected by digital thermometer using thermistor cable connector jack. The polished sample of dimensions 5 mm × 2 mm × 2 mm was chosen for the study. The sample is fixed on the main prism by using methylene iodide as a contact material. The external light from sodium lamp was reflected on the mirror and fallen on the sample. While observing to the eyepiece, the micrometric screw is adjusted to set the scale indication approximately to the refractive index shown on the test piece. The refractive index of urea salicylic acid crystal at 26 °C is measured as 1.457.

Third order non-linear optical measurements: The third order non-linearities of urea salicylic acid crystal were investigated by Z-scan method with He-Ne laser of wavelength of 632.8 nm. The laser beam was focused with the help of a convex lens of focal length 12 cm to give the intensity of 3.13 MW/cm^2 at the focus (Z = 0). The energy transmitted through an aperture is recorded as a function of the sample position. Fig. 3(a) shows the normalized transmission for the open aperture of urea salicylic acid crystal. The non-linear absorption coefficient was estimated using the relation:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}$$

where ΔT = valley value at the open aperture Z-scan curve. I_0 = intensity of the laser beam at focus (Z = 0) and L_{eff} = effective thickness of the sample. From the open aperture Z-scan curve, it can be concluded that as the minimum lies near the focus (Z = 0) and the urea salicylic acid sample exhibits two photon absorption property. The non-linear absorption coefficient (β) is measured as 1.4052 × 10^{-5} cm/W.

Fig. 3(b) illustrates the closed aperture Z-scan profile of the sample. The normalized closed aperture Z-scan curve exhibits a pre-focal transmittance maximum (peak) followed by a post-focal transmittance minimum (valley) signature for the samples which is the sign of negative non-linearity. The

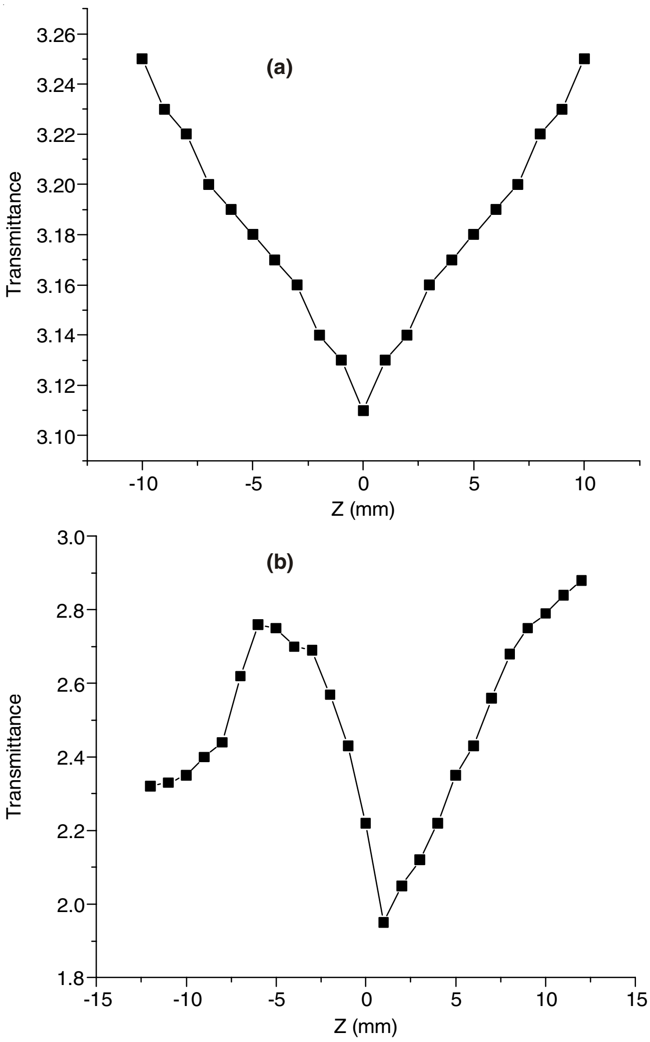

Fig. 3. (a) Open aperture curve of urea salicylic acid crystal, (b) Closed aperture curve of urea salicylic acid crystal

negative non-linear refractive index (n_2) is calculated as -2.9963 × 10^{-11} cm^2/W using the relation,

$$n_2 = \frac{\Delta\phi}{K I_0 L_{eff}} \quad \text{where} \quad \Delta\phi = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}}$$

ΔT_{p-v} = difference between the peak and valley transmission which is written in terms of the on axis phase shift at the focus. S = aperture linear transmittance and is calculated using the relation,

$$S = 1 - \exp\left(\frac{-2r_0^2}{\omega_0^2}\right)$$

where r_0 = radius of the aperture and ω_0 = beam radius at the aperture. And $K = \frac{2\pi}{\lambda}$ (λ = laser wavelength). This peak-valley signature indicates the self-defocussing property of urea salicylic acid crystal which is an essential property for the application in the protection of optical sensors, such as night vision devices [15,16].

The real and imaginary parts of the third order non-linear optical susceptibility $\chi^{(3)}$ are defined as

$$\text{Re}\,\chi^{(3)}\,(\text{esu}) = 10^{-4}\,(\varepsilon_0\, c^2\, n_0^2\, n_2)/\pi$$

$$\text{Im}\ \chi^{(3)}\ (\text{esu}) = 10^{-2}\ (\varepsilon_0\ c^2\ n_0^2\ \lambda\beta)/4\pi^2$$

where ε_0 = vaccum permittivity, n_0 = linear refractive index and c = velocity of light in vaccum. The third order susceptibility of urea salicylic acid is 3.8123×10^{-5} esu. Table-1 portrays the experimental details and the results of the Z-scan technique for urea salicylic acid crystal.

TABLE-1
MEASUREMENT DETAILS AND RESULTS OF Z-SCAN TECHNIQUE

Laser wavelength	632.8 nm
Laser focal length (f)	12 cm
Optical path distance (Z)	115 cm
Spot size diameter in front of the aperture (ω_0)	1 cm
Aperture radius (r_0)	4 mm
Incident intensity at the focus (Z = 0)	3.13 MW/cm^2
Effective thickness (L_{eff})	2.09 mm
Linear refractive index (n_0)	1.457
Non-linear refractive index (n_2)	-2.9963×10^{-11} cm^2/W
Non-linear absorption coefficient (β)	1.4052×10^{-5} cm/W
Third order susceptibility ($\chi^{(3)}$)	3.8123×10^{-5} esu

Conclusion

The optically good quality single crystal of urea salicylic acid has been successfully grown by slow evaporation technique from the mixed solvent of ethanol and water with equal molar ratio at room temperature. The formation of urea salicylic acid is confirmed by single X-ray diffraction study. From UV-visible transmission spectrum, it is evident that urea salicylic acid crystal has a lower cutoff wavelength at 347 nm, which is a good optical window material. The self-defocussing nature and two photon absorption process of the grown urea salicylic acid crystal were confirmed from Z-scan technique. Thus urea salicylic acid crystal is a suitable candidate for optoelectronic applications.

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