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THIRD ORDER NONLINEAR OPTICAL PROPERTIES OF ORGANIC 4-CHLOROANILINIUM 2-CARBOXY ACETATE (CACA) CRYSTAL

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ABSTRACT

The organic nonlinear optical (NLO) material 4-chloroanilinium 2-carboxy acetate (CACA) was grown by slow evaporation solution technique using ethanol as solvent. The crystallinity and crystal structure of the grown crystal were characterized by single and powder X-ray diffraction (XRD) studies. The optical transmission study was observed by UV-vis-NIR spectrum, which indicates that the grown crystal is a good optical transmission window for photonic applications. The third order nonlinear optical properties are derived from Z-scan technique.

Key words: Slow evaporation method, X-ray diffraction analyses, UV-vis-NIR spectral analysis, Z-scan technique.

INTRODUCTION

Nonlinear optical (NLO) materials capable of generating the second harmonic frequency play an important role in the domain of optoelectronics and photonics[1-3]. In recent years, organic NLO materials are attracting a great deal of attention for possible use in optical devices because of their large optical nonlinearity, low cut-off wavelengths, fast response time and high thresholds for laser power[4,5]. Most of the organic molecules show large nonlinear optical response, with the electron-donor and electron-acceptor groups located at the extreme of a system involving correlated and high delocalized π electron states[3,6]. The grown material 4-chloroanilinium 2-carboxyacetate shows nonlinear optical properties due to delocalized π electron states in the asymmetric unit, which contains one 4-chloroanilinium cation and one 2-carboxyacetate anion. It has been recognized that the two-photon optical properties of materials should be affected by the donor–acceptor strength,

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the molecular structure, the conjugation length and the intermolecular charge transfer (ICT) etc.[7-9] The Z-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for separately determining the nonlinear changes in index and changes in absorption. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the interpretation. The signs and magnitudes of third nonlinear optical properties are interpreted in this method[10]. In the present work, the organic 4-chloroanilinium 2-carboxyacetate (CACA) crystal was grown by slow evaporation method using ethanol as solvent. The crystallinity, linear and nonlinear optical properties of the grown CACA crystal are explained in detail.

EXPERIMENTAL

Materials and methods

The organic 4-chloroaniline 2-carboxyacetate (CACA) crystal was synthesized by dissolving in equal molar ratio of malonic acid (10 mmol) and 4-chloroaniline (10 mmol) in the solvent of ethanol. The calculated amount of salts were stirred well for hours 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. Colourless crystals were obtained after 7 days. The grown crystals are shown in Fig. 1.

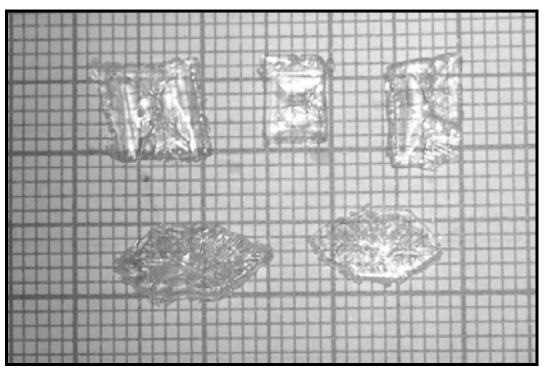

Fig. 1: As grown crystals of CACA

RESULTS AND DISCUSSION

X-Ray diffraction analyses

In order to determine the structure of CACA crystal, single crystal XRD study was carried out using BRUKER AXS diffractometer with Mo Kα (λ = 0.7107 Å) radiation The single crystal X-ray diffraction study was carried out for the grown CACA crystal. The CACA crystal was found to crystallize in monoclinic structure of centrosymmetric space group $P2_{1/C}$ with a = 12.825 Å,

b = 9.224 Å, c = 8.408 Å, β = 93.841^0, V = 992.474 Å^3 and Z = 4. The calculated unit cell parameters of CACA crystal are in good agreement with the reported data[11]. The powdered sample of the grown crystal CACA was characterized using Siemens D500 X-ray diffractometer with Cu Kα (λ = 1.5418 Å) radiation. Intensities for the diffraction peaks were recorded over the range of 2θ from 20^0 to 70^0. The powder X-ray diffraction study of CACA crystalline sample was carried out and the X-ray diffraction pattern for the grown sample is shown in Fig. 2. The well-defined Bragg's peaks at specific 2θ angles have shown high crystallinity of CACA. The lattice parameters from powder XRD pattern are evaluated and peak indexing were carried out using the software Proszki Version 2.4.

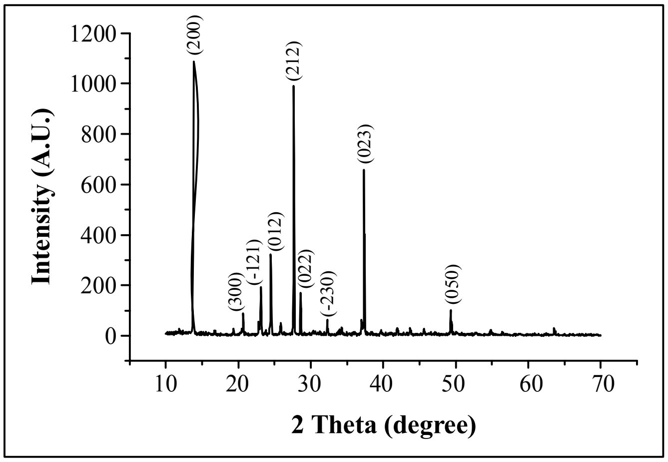

Fig. 2: Powder X-ray diffractogram of CACA crystalline sample

FTIR Analysis

The infrared spectral analysis is effectively used to understand the chemical bonding and is providing information about molecular structure of the synthesized compound. The FTIR spectrum of the sample was recorded using KBr pellet technique in the range of 4000 cm^{-1} – 400 cm^{-1} using Perkin Elmer FTIR Spectrometer. The FT-IR spectrum of CACA is shown in Fig. 3. The peaks at 3405 cm^{-1} and 3131 cm^{-1} show the presence of NH_3 stretching[12] of the grown material. The carboxylic acid C=O and O-H stretching are presented at the peak values of 2957 cm^{-1} and 2564 cm^{-1}, respectively. The peaks at 817 cm^{-1} and 670 cm^{-1} [13] are indicating the presence of chlorine in the compound. The group assignments are shown in Table 1, which confirm the chemical structure of the grown crystal.

Table 1: FTIR assignment for CACA crystalline sample

Wavenumber (cm^{-1})	Assignment
3405, 3131	NH_3 stretching
2957	Carboxylic acid C=O stretching
2564	O-H Stretching
1909	C=O stretching
1688	C-O stretching
1559	C=C stretching
1413	CH_2-C(=O) stretching
1092	C-OH Stretching
899	C-H deformation
817, 670	CH_3=C-Cl stretching

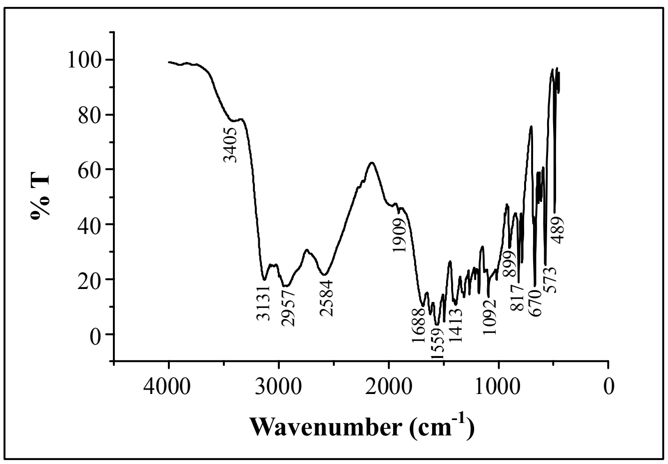

Fig. 3: FTIR spectrum of CACA crystalline sample

UV-vis-NIR Transmittance study

For optical device fabrications, the crystal should have high transparency in a considerable region of wavelength[14-16]. The UV-vis-NIR optical transmittance spectrum of CACA crystal was recorded using Labindia 3032 UV-vis-NIR spectrophotometer with thickness of 1 mm in the range of 190-900 nm. The transmittance spectrum of the title crystal is shown in Fig. 4 (a). From the transmittance spectrum. It is clear that the grown crystal has good transmission in the entire range between 190 nm and 900 nm. The cut off wavelength (λ_c) is found to be 335 nm. The calculated band gap value of the grown CACA crystal is 3.708 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 is the thickness of the crystal. The extinction coefficient (K) is calculated as $K = \frac{\lambda\alpha}{4\pi}$ where λ is the wavelength of the radiation. The reflectance (R) in terms of absorption coefficient (α) can be obtained as –

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

The Figs. 4 (b) and 4 (c) illustrate the dependence of extinction coefficient (K) and reflectance (R) on the wavelength of the grown CACA crystal. 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 1.3405 at the cut off wavelength (λ_c = 335 nm). The Fig. 4 (d) shows the Tauc's plot [hν versus $(\alpha h\nu)^2$] of the CACA crystal, where α is the absorption coefficient and $h\nu$ is the photon energy. The band gap energy as determined from the Tauc's plot is found to be 3.69 eV, which is matched with the observed value of band gap from transmission spectrum. This indicates that CACA is a higher band-gap energy material. As there is no change in the transmission in the entire visible region, it is an advantage as it is the key requirement for materials having NLO properties[17].

Z-Scan technique

The third order nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) were evaluated by the Z-scan technique. In this method the sample is translated in the z-direction along the axis of the focused Gaussian beam from the He-Ne laser at 632.8 nm and the far field intensity is measured as a function of the sample position. Two methods (open and closed aperture) are used for the measurements of nonlinear absorption coefficient (β) and nonlinear refractive index (n_2)[18]. The Fig. 5 (a) and 5 (b) are shown the closed and open Z-scan aperture curve of the grown CACA crystal. The nonlinear optical coefficients n_2, β and χ^3 were calculated using the standard equations[19]. The peak followed by a valley-normalized transmittance obtained from the closed-aperture curve indicates that the sign of the nonlinear refraction (NLR) is negative, which results from the self-defocusing effect[20,21]. In general, the nonlinear absorption was categorized into (1) saturation absorption (SA), where the transmittance of the sample increases with increasing the optical intensity and (2) reverse saturation absorption (RSA) where the transmittance decreases while increasing the optical intensity. The later includes two-photon and multi-photon absorption[22,21]. It is observed that the nonlinear absorption is endorsed to two photon absorption, while the nonlinear refraction is led to self-defocussing. This property is the essential requirement for the protection parts of optical sensors such as night vision devices[23,24]. The promising third order nonlinear optical properties of CACA crystal are discussed in Table 2, suggesting its suitability for application in optical limiting and photonic devices.

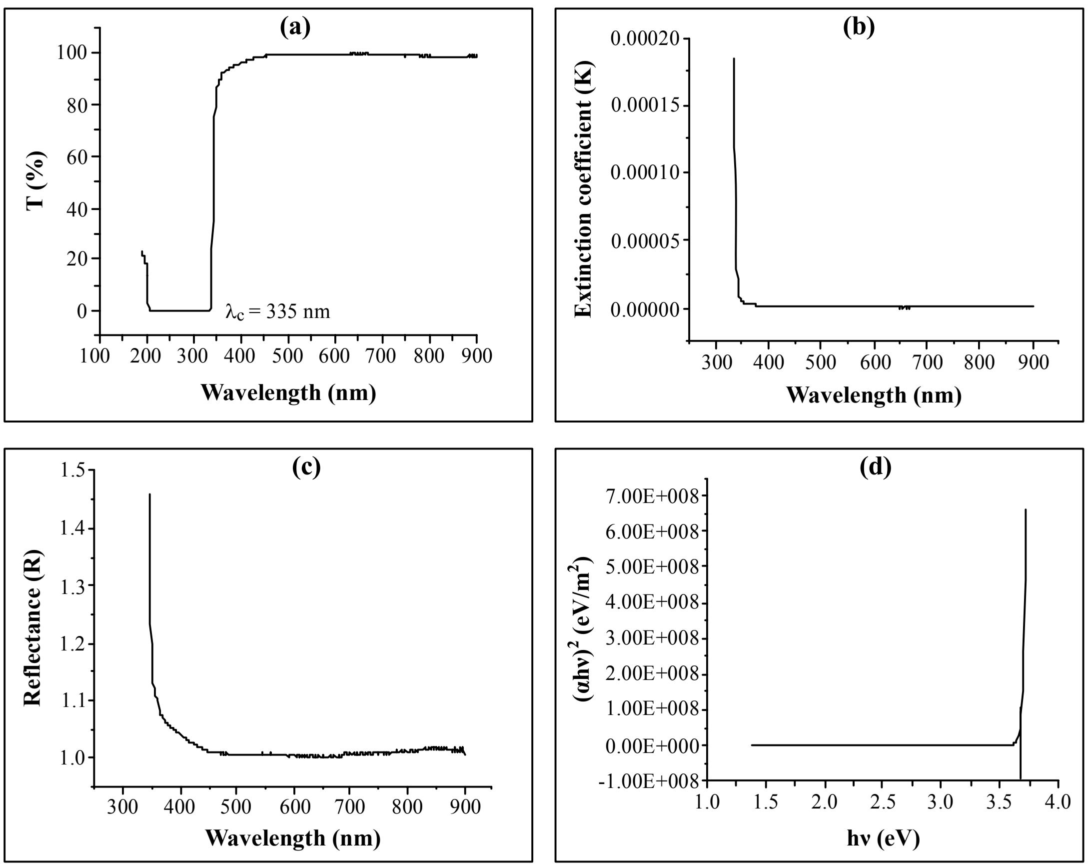

Fig. 4: (a) UV-vis-NIR transmittance spectrum, (b) Extinction coefficient vs wavelength, (c) Reflectance vs wavelength and (d) Tauc's plot of CACA crystal

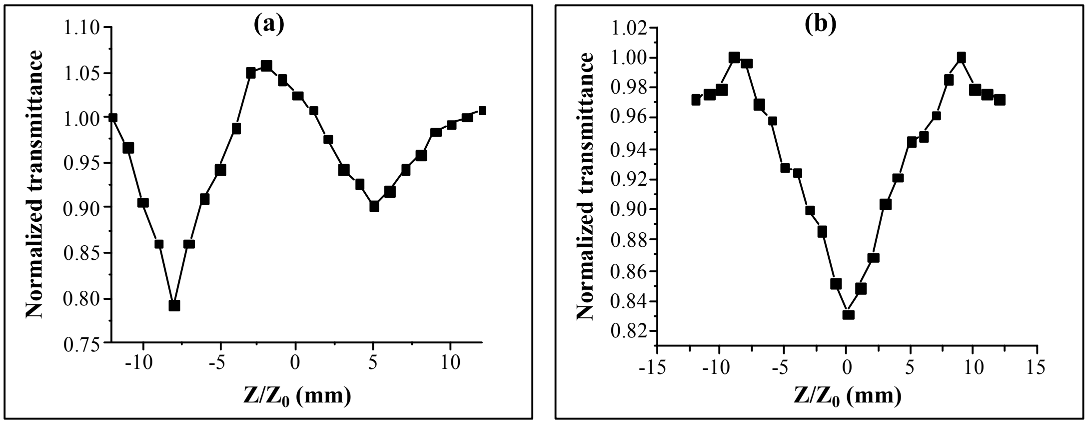

Fig. 5: Z scan curve of CACA crystal for (a) closed aperture and (b) open aperture of CACA

Table 2: 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 absorption coefficient (α)	0.0118
Linear refractive index (n_0)	1.3405
Nonlinear refractive index (n_2)	-2.659×10^{-11} cm^2/W
Nonlinear absorption coefficient (β)	1.2616×10^{-5} cm/W
Third order susceptibility ($\chi^{(3)}$)	3.1408×10^{-9}esu

CONCLUSION

Single crystal of CACA was obtained by slow evaporation method using ethanol as solvent at 333 K. From XRD studies, it is known that the CACA crystal is found to crystallize in monoclinic structure of centrosymmetric space group $P2_1/c$. The vibrational frequencies were identified and assigned from FTIR spectral analysis, which confirm the presence of functional groups of the CACA crystal. The UV-vis-NIR spectrum of CACA crystal shows that it is transparent in the range of 335-900 nm. The grown crystal has the lower cutoff wavelength of 335 nm, which is sufficient for photonic applications. The band gap of the grown material was calculated as 3.70 eV. The third order nonlinear optical properties reveal that the grown crystal CACA is a potential candidate for the fabrication of electro-optic, non-linear optical and optoelectronic devices.

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