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Nonlinear optical, optical limiting and dielectric properties of organic cyclohexylammonium acetate single crystal

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ABSTRACT

We report the growth and nonlinear optical properties of cyclohexylammonium acetate (CYHAC) crystal. The functional groups and crystal structure were determined using FT-IR analyses and single crystal XRD (293 K). UV–Vis–NIR measures the cutoff wavelength (254 nm) and optical band gap (5.17 eV) of CYHAC crystal. TG-DSC spectrum shows the melting point (161 °C) and decomposition of the compound. Activation energy was calculated from dielectric studies as a function of frequency at different temperatures. Laser damage threshold of CYHAC is 5.23 GW/cm^2. Nonlinear optical parameters were calculated using Z-Scan technique for this material and its optical limiting behavior were also tested, the value of limiting threshold and clamping output are 24.3 mW and 7.1 mW respectively.

1. Introduction

The materials with high nonlinear optical response play a vital role in optical information processing, optoelectronic applications, integrated optics and waveguide device. Both organic and inorganic materials are still developed for the applications of optical switching and frequency doubling [1,2]. However organic materials afford larger degrees of flexibilities with respect to architecture, high nonlinear coefficients, design and processing as compared to inorganic materials [3]. Organic materials are required for the applications in the field of photonics, ultrafast optical switches due to their nonlinear optical behavior [4–6]. Carboxylic acids constitute suitable building blocks which can make variety of possibilities for molecular assembly through the hydrogen bonded networks [7]. Due to combination of strength and directionality, hydrogen bond interactions potentially more concerned in crystal engineering field [8]. The organic cyclohexylammonium acetate single crystal (CYHAC) was grown by slow evaporation technique. The present work deals with its physical properties like structural, optical, thermal stability, third order nonlinear optical and optical limiting behavior.

2. Experimental procedure

2.1. Crystal growth

The CYHAC single crystal was grown by slow evaporation technique taking equimolar ratio of cyclohexylamine (5.74 mL, 50 mmol) and acetic acid (2.86 mL, 50 mmol) in 30 mL of water. The mixed solution was stirred 24 h to attain homogeneity. The solution was filtered and was kept in undisturbed place. After 15 days CYHAC single crystal was harvested from the mother solution (Fig. 1a).

3. Results and discussion

3.1. Single crystal XRD analysis

The structure of CYHAC was solved using single crystal XRD at 293 K by direct method and was refined by full matrix least square method using SHELXL program. It was observed that the crystal belongs to monoclinic system and cell parameters are given in Table 1.

3.2. FT-IR studies

FT-IR study is a very useful tool for the identification of functional groups present in the compound which is shown in

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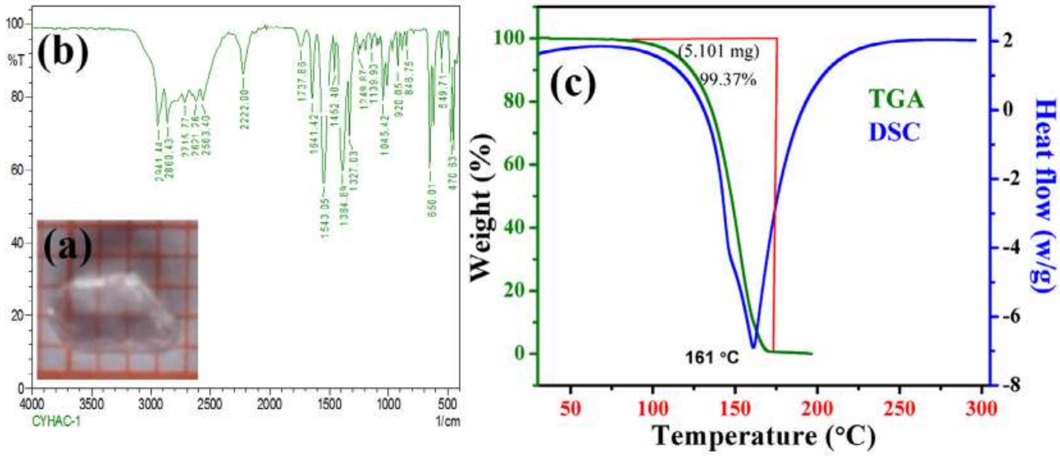

Fig. 1. (a) As grown crystal, (b) FT-IR of CYHAC crystal and (c) TG-DSC spectrum of CYHAC crystal.

Table 1
Crystal data of CYHAC.

Chemical formula	$C_8H_{17}NO_2$
Formula weight	159.22
Wavelength	0.71073
a (Å)	23.8840(2)
b (Å)	6.4202(5)
c (Å)	16.3212(17)
β (°)	131.836(4)
Volume ($Å^3$)	1864.7(3)
T/K	293(2)
Z	8
ρ (g/cm^3)	1.134
Space group	Monoclinic *C*2/*c*
Absorption coefficient	0.080
F(0 0 0)	704
Crystal size	0.10 × 0.15 × 0.20 mm
Theta range for data collection	2.289–30.858
Limiting Indices	$-34 \le h \le 33$, $-9 \le k \le 9$, $-23 \le l \le 23$
Refinement	
R(all), *R*(gt)	0.1076, 0.0519
w*R*(ref), w*R*(gt)	0.1623, 0.1333
Reflections/Restraints/parameters	2904/0/128
$\Delta\rho_{max}$, $\Delta\rho_{min}$, $(\Delta/\sigma)_{max}$	0.274, −0.205, 0.050
CCDC No:	1551079

Fig. 1b. The peaks at 2941–2860 cm^{-1} and 1139 cm^{-1} indicate CH stretching and C—C—O stretching [9]. The presence of C═O stretching at 1641 cm^{-1} and C—O stretching at 1384 cm^{-1} confirms the carboxylate anion present in the crystal. The peaks at 1543 cm^{-1}, 1452 cm^{-1} and 1249 cm^{-1} indicate NH_3^+symmetrical bending, COO^- symmetrical stretching and COO^- vibrations respectively [10].

3.3. UV–Vis–NIR analysis

The UV–Vis–NIR spectrum of CYHAC was recorded in the range of 200–700 nm using Jasco-V-670 spectrometer. The cut off wavelength was found to be 254 nm and it occurs due to the electronic transition from non-bonding to anti-bonding orbital (n → π*, acetate ion to cyclohexylammonium ion). Band gap of CYHAC was calculated and the value is 5.17 eV.

3.4. Thermal analysis

The thermal stability and composition of the sample were determined by thermo gravimetric analysis (TGA) and differential scanning colorimetry (DSC) analysis [11]. The TGA-DSC analysis of CYHAC was carried out in the range of 30–300 °C at a heating rate of 20 °C/min in nitrogen atmosphere (Fig. 1c). Initially 5.1330 mg weight of CYHAC was used for the analysis. From Fig. 1c, 99.37% weight loss (5.101 mg) occurred over a temperature from 120 to 170 °C with final residue of 0.63% (0.032 mg). A sharp endothermic peak at 161 °C observed from the DSC curve indicates the melting point of the compound. Nonexistence of endothermic or exothermic peaks before the melting point concludes that the material is suitable candidate for nonlinear optical applications up to its melting point.

3.5. Dielectric studies

The dielectric studies were carried out using Numetric Q impedance analyzer in the frequency range of 100 Hz–5 MHz. Fig. 2a and b shows the normal trend of dielectric materials behavior. The ε_r decreases with increase in frequency (f) is due to the electrical relaxation process and high value of ε_r at low frequency is due to the superimposition of material electrode interface polarization with other relaxation process [12]. The AC conductivity was calculated using $\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta$ [13], where ε_0 is permittivity of free space. Two different conductivity patterns were observed which is in Fig. 2c. At low frequency region the conductivity has frequency-independent nature (plateau region) which is due to the activated hopping of ions and it has frequency-dependent conductivity at high frequency region (dispersion region). The activation energy was calculated by plotting the graph between $\ln_{ac}$ and 1000/T (Fig. 2d) using the relation $\sigma_{ac} = \sigma_0 \exp(\frac{-E_a}{kT})$, where k is the Boltzmann constant, E_a is the activation energy and T is absolute temperature. The calculated E_a at 100 Hz, 500 Hz, 1 KHz, 5 KHZ and 10 KHz are 0.098 eV, 0.132 eV, 0.154 eV, 0.329 eV and 0.491 eV respectively.

3.6. Laser damage threshold studies

Laser damage threshold (LDT) of CYHAC was measured by Q-switched Nd:YAG Laser (1064 nm) with 0.8 mm laser beam diameter. LDT was calculated using $I = E/\tau\pi r^2$, here, I is the energy density, E is the input energy (mJ), τ is pulse width (10 ns) and r is the radius of laser spot (cm^2). I was calculated (5.23 GW/cm^2) and it is revealed that the material can withstand up to 5.23 GW/cm^2 which is suitable for high power frequency applications.

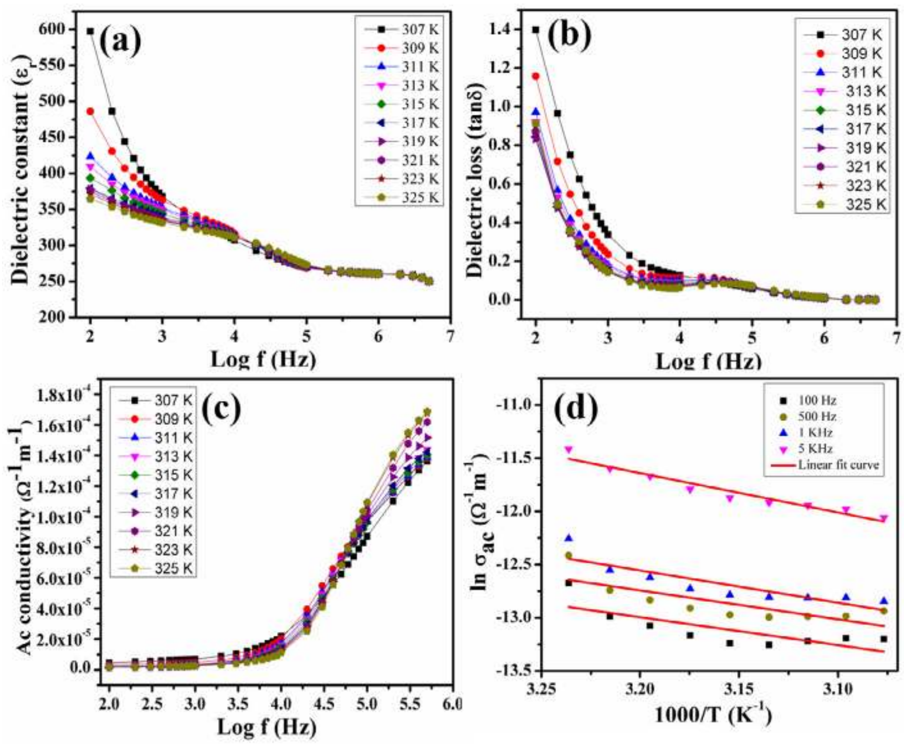

Fig. 2. (a) Dielectric constant, (b) Dielectric loss, (c) AC conductivity and (d) 1000/T vs ln σ_{ac}.

3.7. Nonlinear optical studies

Z-scan is a simple and familiar technique to determine the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) simultaneously. The sample was translated through Gaussian beam along Z direction, using diode pumped cw Nd:YAG Laser (Coherent CompassTM215M-50 at 532 nm) with 3.5 cm focal length and far field intensity was measured as a function of sample position. From the closed aperture curve (Fig. 3a) n_2 was calculated using the relation

$$n_2 = \frac{\Delta\Phi}{KI_0L_{eff}} \qquad (1)$$

where $\Delta\Phi$ is phase shift, K is wave vector, I_0 is intensity of laser beam and L_{eff} is the effective thickness of the sample. Nonlinear absorption coefficient was calculated from open aperture curve (Fig. 3b) using

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \qquad (2)$$

where ΔT is valley value at open aperture curve. The real and imaginary part of the third order nonlinear susceptibility ($\chi^{(3)}$) were calculated by,

$$R_e(\chi^{(3)})esu = \frac{10^{-4}\varepsilon_0 c^2 n_0^2 n_2}{\pi}\ \mathrm{cm^2\ W^{-1}} \qquad (3)$$

$$I_m(\chi^{(3)})esu = \frac{10^{-2}\varepsilon_0 c^2 n_0^2 \lambda\beta}{4\pi^2}\ \mathrm{cm^2\ W^{-1}} \qquad (4)$$

Here ε_0 is the vacuum permittivity, c is the velocity of light and n_0 is the linear refractive index of the crystal. The ($\chi^{(3)}$) was calculated using the relation [14],

$$|\chi^{(3)}| = \left[\left(R_e(\chi^{(3)})\right)^2 + \left(I_m(\chi^{(3)})\right)^2\right]^1/2 \qquad (5)$$

The peak followed by the valley represents the negative sign of nonlinear refractive index which is due to the self-defocusing effect. When the sample approaches focus, transmittance either decreases or increases which forms a valley (reverse saturable absorption) or peak (saturable absorption) at the focus. It is clear that CYHAC exhibits saturable absorption. Fig. 3c shows the ratio of closed to open aperture curve. The nonlinear refractive index, nonlinear absorption coefficient and nonlinear optical susceptibility of the compound are -4.920×10^{-8} cm^2 W^{-1}, 0.080×10^{-4} cm/W and 2.394×10^{-6} esu respectively and $\chi^{(3)}$ is superior than some other organic compounds [15,16]. Optical limiting (OL) behavior was tested using 532 nm diode pumped Nd:YAG laser in the range of 0.45–0.47 mW and it is due to the nonlinear refraction of the materials [17]. From Fig. 3d, it was found that the intensity of output transmittance varies linearly at low input intensity. Further increasing the input power, the output transmittance reaches plateau and beyond 24.3 mW it is saturated which shows the obvious limiting amplitude. The threshold limiting and output clamping were found to be 24.3 mW and 7.1 mW respectively. The maximum output power of CYHAC shows the limiting behavior, hence it is suitable for optical limiting applications.

4. Conclusion

A new nonlinear optical CYHAC crystal was grown by slow evaporation technique and it belongs to monoclinic system with centro-symmetric space group ($C2/c$). The functional group (NH_3^+, COO^-) which is present in the compound was confirmed by FT-IR analysis. The cut off wavelength (254 nm) and energy gap (5.17 eV) were found using UV–Vis-NIR spectrum. Thermal analysis revealed that CYHAC compound was stable up to 161 °C. The dielectric studies revealed the presence of interface polarization and dipole relaxation in the sample. The low value of dielectric loss indicated the good quality of crystal which is suitable for nonlinear optical applications and the AC conductivity was increased with

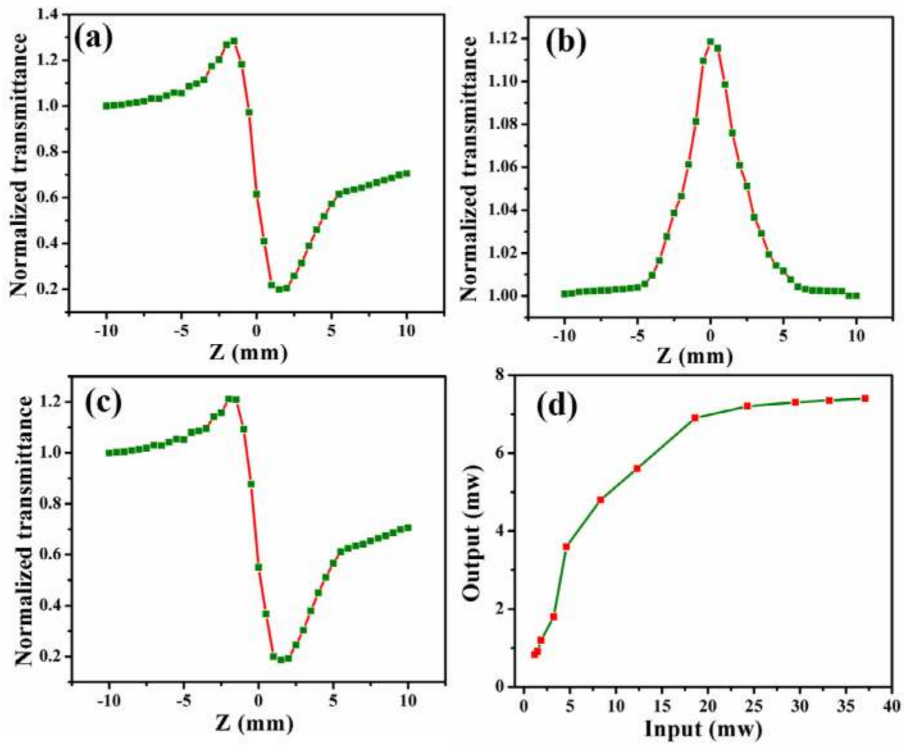

Fig. 3. (a) Closed aperture, (b) open aperture, (c) ratio of closed to open aperture curve and (d) OL spectrum.

increase in frequency and temperature. LDT of CYHAC is 5.23 GW/cm^2 which is suitable for high power frequency applications. Z scan spectrum shows the strong saturation absorption and self-defocusing effect which gives negative sign of n_2. The large nonlinear response of CYHAC shows a strong limiting behavior at 532 nm. Optical limiting of compound mainly attributed to self-defocusing effect. Hence the CYHAC material is promising candidate for nonlinear optical applications.

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