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Crystal growth and characterization of 2-amino-4,6-dimethylpyrimidium 3,5-dinitrobenzoate dihydrate (2APDBD) single crystal for Nonlinear optical (NLO) application

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ABSTRACT

Single crystal of 2-amino-4,6-dimethylpyrimidium 3,5-dinitrobenzoate dihydrate (2APDBD) was grown by solution growth technique. The X-ray diffraction reveals that 2APDBD crystal belongs to a centrosymmetric triclinic crystal system with space group P-1. The UV visible-NIR spectra confirm a peak at 350 nm with lower cut off wavelength shows a wide transmission window in the entire visible region. The electrical characteristics of 2APDBD crystal have a low density of defects and a low value of dielectric loss found from the dielectric studies. To find out the third order nonlinear susceptibilities ($\chi^{(3)}$) Z-can analysis was used.

1. Introduction

A lot of research is done on the organic NLO crystal, which has high laser damage thresholds and second- and third-order nonlinear properties. It is indicated that organic NLO crystals are promising candidates for several applications due to their specific novel physicochemical properties. The remarkable contribution has paid attention to optical materials for the fabrication of optoelectronic devices. The materials developed over the past decade facilitate their non-linear applications in optical information processing, optical communication, data storage, and optical transmission system [1]. Researchers working on organic materials discovered phenomenal properties that exhibit a high degree of delocalization due to their weak Vander-walls and hydrogen bonds combined with π electrons, low cut-off wavelength in the UV region, which enhanced large optical non-linearity in optical devices for their rapid response, flexibility, and capability of designing compounds [2]. Researchers have explored various novel NLO complexes produced through the coupling of different organic molecules as a result of their ongoing research on organic NLO materials. 2-Amino-4,6-dimethyl-pyrimidinium 3,5-dinitro-benzoate dihydrate (1:1) organic NLO single crystal has been reported by A. Subashini et.al., [3]. Pyrimidines and aminopyrimidine derivatives are physiologically significant chemicals that occur naturally as components of nucleic acids. Nucleic acid activities can be determined by hydrogen bonding patterns, which include base pairing, which is responsible for genetic information transfer [4]. 3,5-Dinitrobenzoic acid has been involved several organic compound [5–7]. The derivative of dinitrobenzoic acid have been initiated to be effective agent as radiation sensitizers in tumour treatment [8]. Furthermore, some synthesised dinitrobenzoate compounds have demonstrated beneficial characteristics in DNA and oligosaccharide structures. There are lots of benefit for these derivatives such as Herbicides, insecticides, pharmaceuticals, food flavourings, feed additives, vitamins, rubber compounds, flavours, disinfectants, explosives, and adhesives are all composed of pyridine and its derivatives [9] . In the present work, 2-amino-4,6-dimethylpyrimidium 3,5-dinitrobenzoate dihydrate (2APDBD) single crystal was grown by SEST. Various characterizations are used to analyse the 2APDBD crystal, such as structural analysis (SXRD, PXRD), optical analysis (UV-Visible-NIR), electrical analysis (dielectric

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constant & dielectric loss), and third harmonic generation (Z-scan).

2. Experimental details

2.1. Synthesis procedure

In the synthesis process, 2-amino-4,6-dimethylpyrimidine (Merck 99%) (5.81 g/mol) was used as a base compound, and 3,5-dinitrobe4nzoic acid (10 g/mol) (Sigma Aldrich, 99%) was used as an acid compound (2APDBD). 2APDBD was collected, and separately dissolved in methanol using a 1:1 stoichiometric ratio, and the solutions were thoroughly mixed using a mechanical stirrer for almost an hour. Figure 1 shows the chemical reaction of title crystal. Using Whatman high-quality filter paper, the accumulated clear orange colour solution was filtered off to remove the suspended impurities and left aside without being mechanically shaken to form crystals in a dust-free environment at room temperature. After 25 days, the excellent transparent 2APDBD molecular adduct single crystals were carefully separated from the mother liquor. In order to get crystals of the highest quality, harvested crystals were repeatedly recrystallized; an image of the 2APDBD crystals is presented in Figure 2 (A).

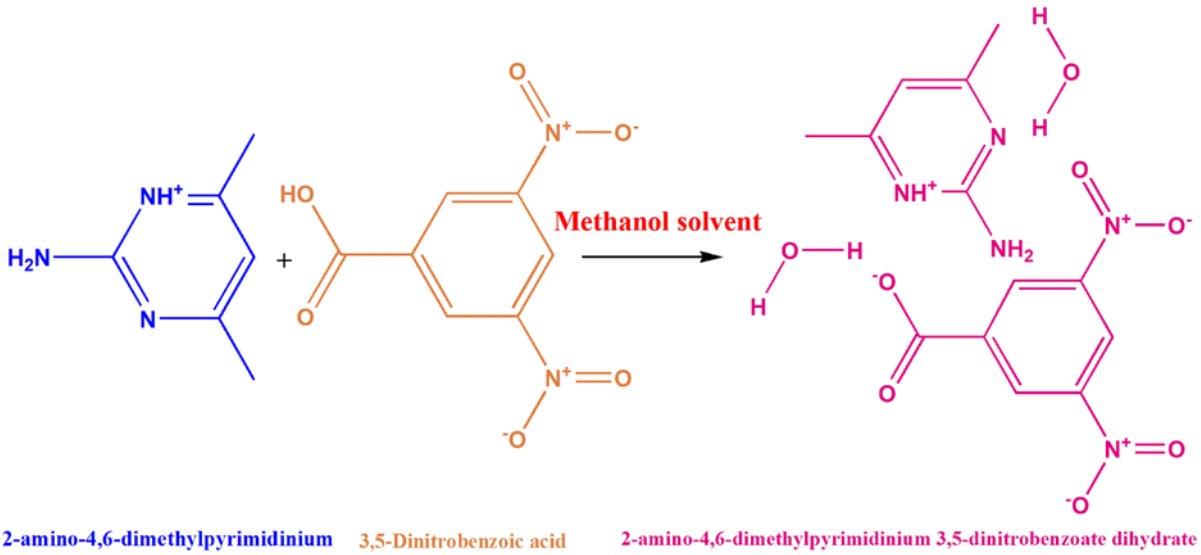

Fig.1. Synthesis reaction scheme of 2APDBD material

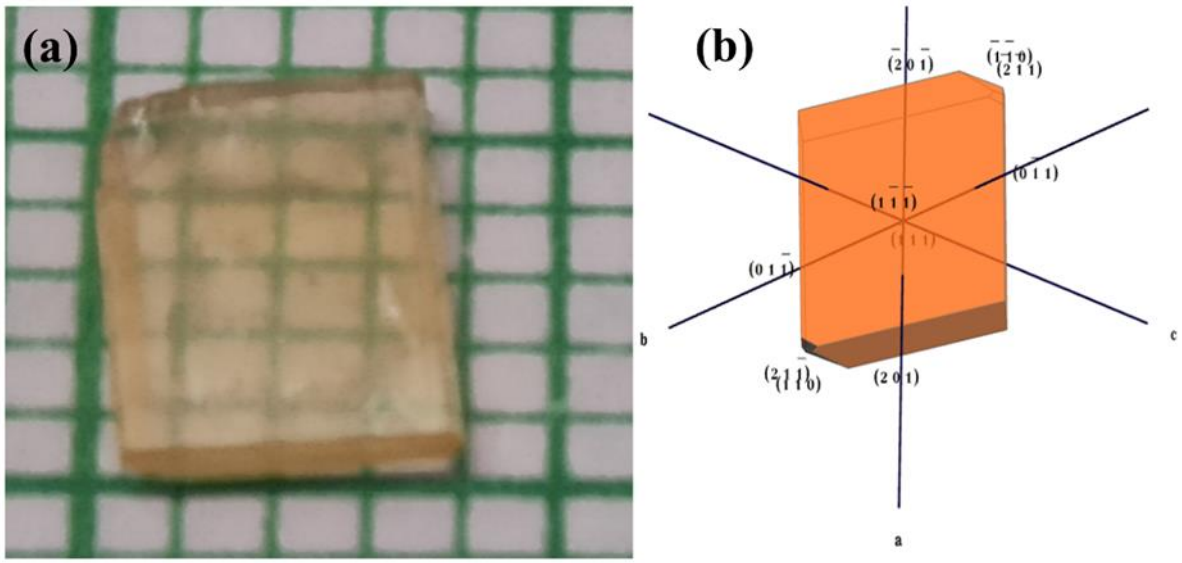

Fig.2. (a) 2APDBD grown crystal 2(b) its morphology

2.2. Characterization studies

A Bruker AXS Kappa APEX II CCD instrument was used to identify the unit cell parameters of the 2APDBD crystal with the radiation of monochromatic (MoKα). PANalytical

X'pert Pro instrument using Cukα radiation was deployed for analyzing the PXRD measurement to find out various diffraction planes. The software used to draw the morphology of the 2APDBD crystal is WinXmorph. The Perkin-Elmer Lambda-35 UV-Visible-NIR spectrophotometer has been used to find out the optical properties of the 2APDBD crystal. An electrical analysis of the 2APDBD crystal was taken using a PSM 1735 LCR meter. The third order NLO properties were determined using the Z-scan method. A continuous wave was used in Z-scan instrument.

3. Results and discussion

3.1. SXRD analysis

SXRD analysis of the synthesised crystal is obtained at room temperature. The unit cell parameters values are a = 7.15 Å, b = 11.02 Å, c = 11.15 Å, α = 99.47º, β = 101.32 º, γ = 100.82 º and V = 837.3 Å^3. 2APDBD belongs to triclinic system with the centrosymmetric space group P-1. The present values are well mated with reported values A. Subashini el. al [3]. Table 1 shows the matched value of 2APDBD with previous reported work.

3.2. PXRD analysis

The various diffraction (h, k, l) planes and the phase purity were identified by the PXRD analysis. The measurements were carried out with 2θ degree ranging from 10º-50º, a step size of 0.050 s and at a scanning time of 5 seconds at ambient temperature. The obtained XRD pattern of title crystal is in good agreement with reported refinement. The fine powder made from the grown 2APDBD crystals by crushing them for about 10 minutes was used for the PXRD measurements. The comparison between CIF data and experimental PXRD spectra is revealed in Figure 3. The high sharp peaks display that the 2APDBD crystal has good crystalline nature. Using the William Hall equation, (Eq.1), the lattice strain of the grown 2APDBD crystal was identified.

$$\beta cos\theta = \frac{K\lambda}{D} + 4\varepsilon\, sin\theta \quad (1)$$

Table 1. Comparison of lattice parameters of 2APDBD crystal

Parameters	A. Subashini et.al [3]	Present work
a	7.14 Å	7.15 Å
b	11.02 Å	11.02 Å
c	11.15 Å	11.15 Å
α	99.47º	99.47º
β	101.32 º	101.32 º
γ	100.83 º	100.82 º
Z	2	
V	827.33 Å^3	
Crystal system	Triclinic	
Space group	P-1	

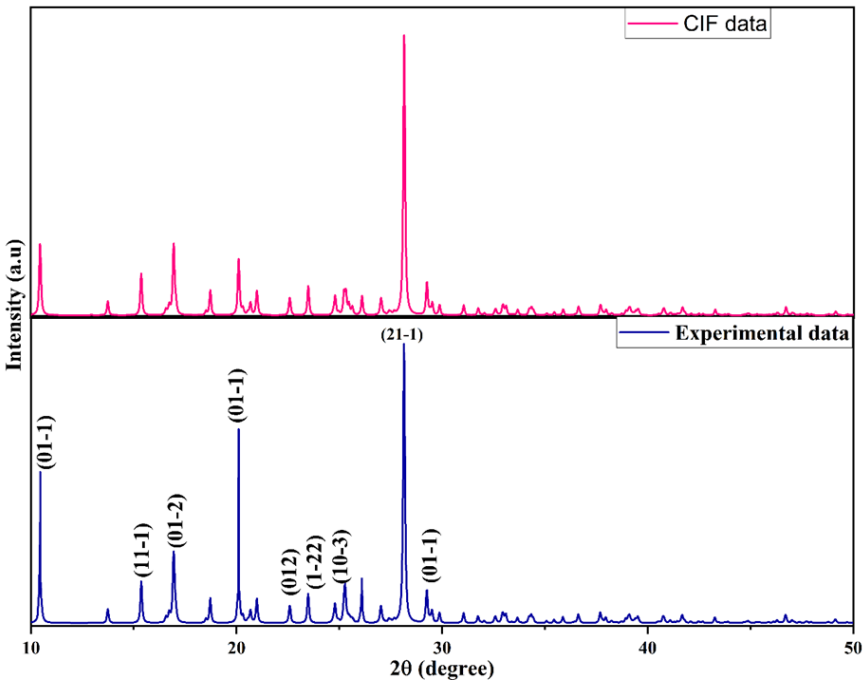

Fig.3. Comparison of PXRD spectra of CIF data and experimental data

where β denotes full width at half maxima, θ represents the Bragg diffraction angle, K represents the Scherrer constant, and λ is the x-ray wavelength.

3.3. UV-Visible-NIR analysis

The transmittance spectrum of the grown 2-amino-4,6-dimethylpyrimidium 3,5-dinitrobenzoate dihydrate is presented in Figure 4 (a). From the UV-Visible spectrum analysis, it is understood that the grown 2APDBD crystal has high transmittance. To enhance low-energy state electron to higher energy states, the NLO crystal typically has very low visible light absorption & good transparency across the near infrared range. These characteristics make the NLO crystal appropriate for NLO-oriented device constructions. The lower cut-off wavelength in the transmittance spectrum of 2APDBD crystal is obtained at 350 nm. The transmittance spectrum brings out all the details about the crystal structure due to the direct interaction of EM wave and the absorption in the region of the UV zone from the n→π* electron transition occurring inside the material by the carbonyl [10]. The absorption coefficient (α) is calculated using transmittance value as well as thickness of the samples; these values are obtained by the following Eq. (2).

$$\alpha = \frac{2.303}{t}\log\frac{1}{T} \tag{2}$$

where 't' represents the thickness of the crystal, which is used for UV-Visible analysis & 'T' is the crystal transmittance percentage. The UV-visible band gap (Eg) was calculated using Tauc's plot Eq. (3)

$$(\alpha h\nu) = A(E_g - h\nu)^{\frac{1}{2}} \tag{3}$$

In the above equation, 'h' represents Planck's constant, 'ν' denotes frequency & 'A' represents a constant. Figure 4(b) shows the Tauc's plot graph among $(\alpha h\nu)^2$ vs (hν). The optical bandgap determined from the Tauc's plot is E_g = 3.5 eV. The 2APDBD crystal has a high transmittance percentage in the visible range, which is useful for optoelectronic applications[10].

3.4. Dielectric analysis

The electrical properties of 2APDBD single crystal were investigated by the dielectric constant and dielectric loss. For calculating the dielectric measurements, the parallel plate capacitance (c) and dissipation factor (δ) were identified. Figure 5 displays both the data on the frequency dependence of the dielectric constant and the dielectric loss. According to Figure 5, the 2APDBD crystal has a high dielectric constant at low frequencies and a decreasing dielectric constant as frequency increases. A well-polished 2APDBD crystal with dimensions of 6 mm in diameter and 1 mm in thickness undertook a dielectric analysis for investigation. The dielectric constant of 2APDBD crystal has been calculated in the frequency range of 10 Hz to 100 Hz and has a silver paste coating on both sides. The grown PMC 2APDBD crystal dielectric constant can usually be determined using the equation below [11].

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A} \tag{4}$$

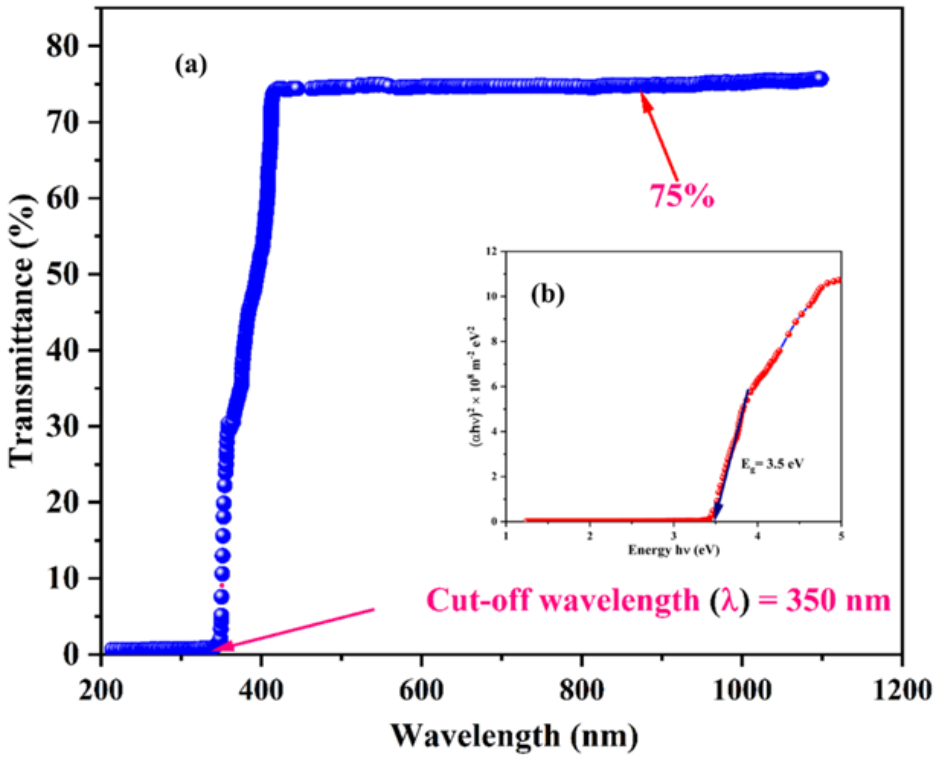

Fig.4. (a) UV-Visible-NIR spectrum of 2APDBD crystal and (b) optical band gap spectrum of 2APDBD crystal

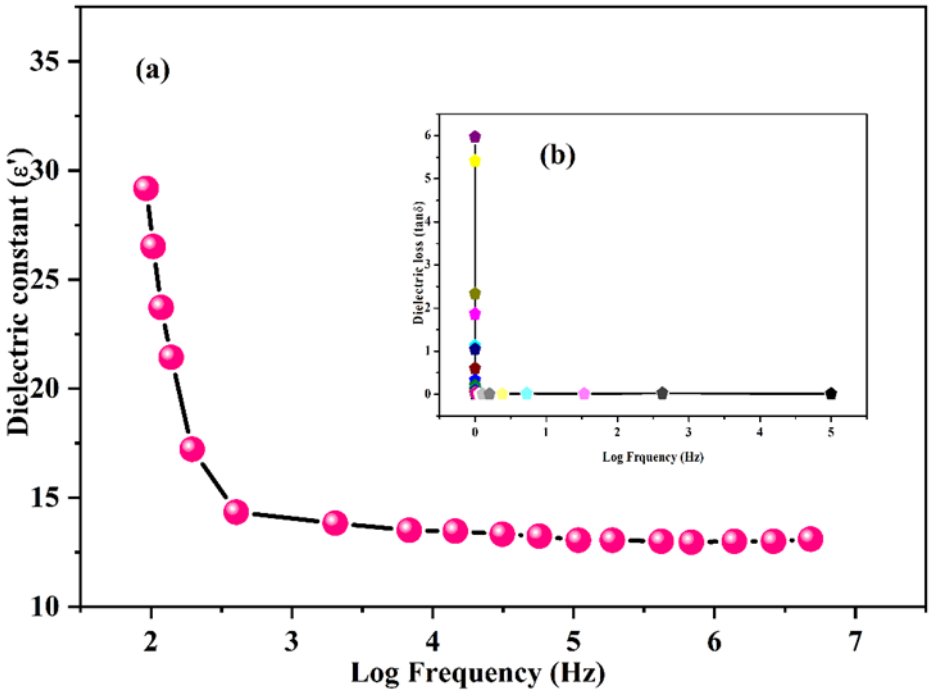

Fig.5. (a) Dielectric constant and (b) dielectric loss spectra of 2APDBD crystal

In the above equation, C_p – parallel capacitor, d - crystal thickness, ε_0 – permittivity, and A – constant. The motive of the low dielectric constant and the high-frequency range were used to estimate the space charges and the orientation of the material as a result of ionised polarisation. Higher frequencies of dielectric constant values result from the electronic polarizations. Considering the dielectric loss, which is mainly the power loss, it implies that very few defects are in as-grown crystal surface. These characteristics lead to the conclusion that the PMC crystal is suitable for photonic and electronic applications.

3.5. Third harmonic generation (Z-scan) analysis

Z-scan is a non-linear intensity measurement technique that involves passing the sample through a focused laser beam for a predetermined amount of time while maintaining the record of any intensity changes. Figure 6 depicts the 2APDBD crystal's open aperture (OA) and closed aperture (CA) spectra.

$$\Delta T_{v-p} = 0.406\,(1-S)^{0.25}|\Delta\phi| \quad (5)$$

where S – aperture linear transmittance and it is used to calculated following relation

$$S = 1 - \exp\left(-\frac{2r_a^2}{\omega_a^2}\right) \quad (6)$$

where r_a – aperture radius and ω_a – beam radius at the aperture. The refractive index (RI) is given as

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \quad (7)$$

Where ΔT indicates the one valley value at the OA Z-scan curve. For saturable absorption and two-photon absorption, the value will be negative and positive, respectively. The definition of the real and imaginary components of the third-order nonlinear optical susceptibility $\chi^{(3)}$ is

$$R_e\chi^{(3)} = \frac{10^{-4}\varepsilon_0 C^2 n_0^2 n_2}{\pi}\left(\frac{cm^2}{W}\right) \quad (8)$$

$$I_m\chi^{(3)} = \frac{10^{-2}\varepsilon_0 C^2 \lambda\beta n_0^2}{4\pi^2}\left(\frac{cm^2}{W}\right), \quad (9)$$

where ε_0 – permittivity of vacuum, n_0 – linear refractive index of the crystal and C – velocity of light in vacuum. The 3rd order NLO susceptibility is the value used to find out the following relation

$$\chi^{(3)} = \sqrt{[R_e(\chi^{(3)})]^2 + [I_m(\chi^{(3)}]^2} \quad (10)$$

From the CA spectrum, pre-focal valley to peak arrangement exhibits that the positive values of non-linear RI, nonlinear RI (n_2), has been determined to be 1.3×10^{-1} cm^2/W. From the results, title crystal has positive refractive index. Which could belong to the grown crystal, associated with the nature of self-focusing nature. Hence, title crystal can be used for optical sensors [12]. The OA Z-scan curve shows that when the minimum is near the focus (Z = 0), the nonlinear absorption is viewed as reverse saturated absorption. The β is found to be 4.3×10^{-4} cm/W. The final value of 3rd order NLO susceptibility is 1.119×10^{-6} esu. The susceptibility value is higher than that of standard KDP, ADP, and even other pyridine derivative crystals. The comparison of optical susceptibility value with other NLO crystals is shown in Table 2.

Table 2. Comparison of Z-scan ($\chi^{(3)}$) of 2APDBD crystal with that of other NLO crystals

Materials	Third order NLO susceptibility (esu)	Reference
2-amino-4,6-dimethylpyrimidium 3,5-dinitrobenzoate dihydrate	1.119×10^{-6}	Present work
2-amino-4,6-dimethylpyrimidine benzoic acid	2.9167×10^{-8}	[13]
2-Amino-4,6-Dimethyl Pyrimidine 4-nitrophenol	2.48×10^{-8}	[14]
Ammonium dihydrogen phosphate	1.81×10^{-14}	[15]
Potassium dihydrogen phosphate	3.72×10^{-14}	[16]

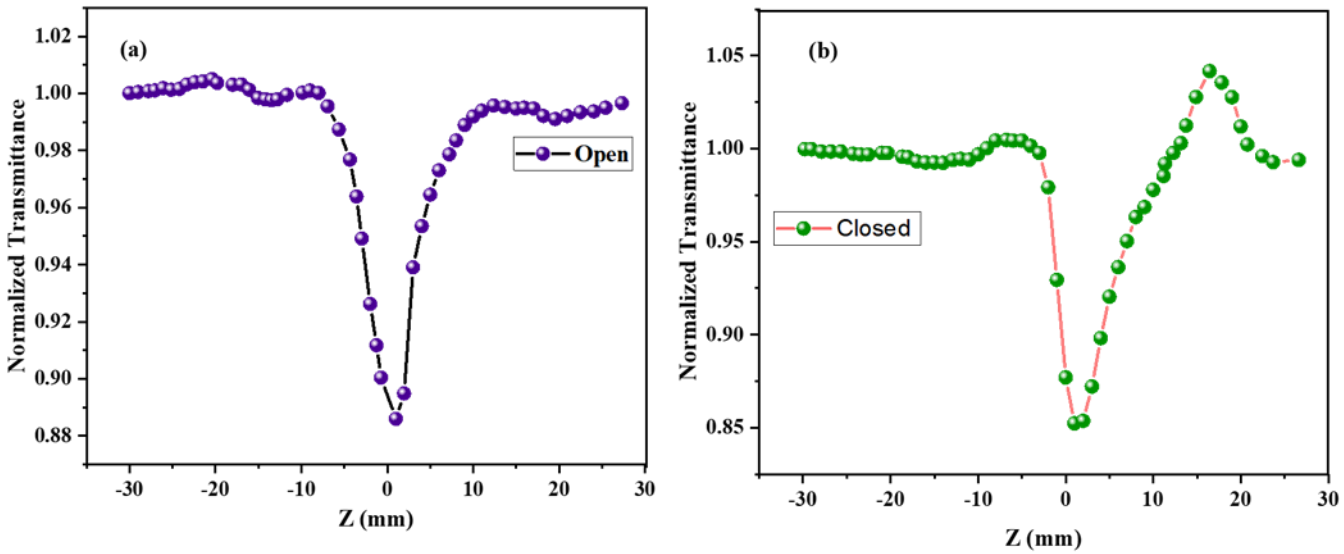

Fig.6. The 2APDBD crystal's open aperture (OA) and Closed aperture (CA) spectra.

4. Conclusion

The single crystal of 2APDBD has successfully been grown by SEST. The 2APDBD crystal is soluble in methanol. The structural properties of the 2APDBD crystal were investigated by SXRD and PXRD analyses. The result of SXRD shows experimental parameter values are exactly matched with reported values. The result of PXRD shows that the sharp peaks denote that the 2APDBD crystal has a good crystalline nature. The optical characteristics of the 2APDBD crystal denote the high transmittance (75%) value and low cutoff wavelength of 350 nm. 2APDBD crystals have very good electrical properties, which are confirmed by the dielectric constant and dielectric loss. Z-scan result exposes that the 2APDBD crystal possesses relatively higher value of nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) leading to larger value of third-order nonlinear optical susceptibility ($\chi^{(3)}$) which is apt for optical limiting applications.

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