

# Investigation of growth, optical properties, polarizability, and photoluminescence behaviour of the NLO single crystal of 1-Carboxy-2-Methylpropan-1-Aminium Chloride 2-Azaniumyl-3-methylbutanoate for Photonic Applications

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**Abstract**—The slow evaporation solution growth method was used to synthesise a nonlinear optical single crystal of 1-Carboxy-2-Methylpropan-1-Aminium Chloride 2-Azaniumyl-3-methylbutanoate using ethanol as solvent. The crystallisation process yielded a well-defined monoclinic system with centrosymmetric nature of  $P2_1$  space group crystal, was revealed by comprehensive of single crystal X-ray diffraction analysis. UV-Vis-NIR spectroscopy, revealing a significant cut-off wavelength of the title compound. Urbach energy, which measures the width of the bandgap tails in semiconductors, showed a low value, indicating that grown crystal has excellent crystallinity, as well as a steepness parameter indicating sharp absorption edges. The electron-phonon interaction energy was estimated, offering insights into the coupling between electronic states and lattice vibrations. The grown material optical constants graphs such as the optical conductivity, extinction coefficient and refractive index were plotted with the function of optical absorption, wavelength and photon energy for assessing optical applications. Photoluminescence analysis demonstrated the excellent structural quality of the grown crystal. The grown compound electronic polarizability was estimated quantitatively, further advancing the understanding of its electro-optic properties. These comprehensive findings suggest that the compound has strong potential for use in nonlinear optical (NLO) devices.

**Index Terms**—Structural refinement, Refractive index, Optical conductivity, electronic polarizability, Photoluminescence.

## I. INTRODUCTION

As society confronts an ever-increasing flow of information, the need for rapid, efficient information processing is growing significantly. At the heart of this technological revolution are electronic and photonic materials, which serve as fundamental pillars for ongoing scientific innovation and advancements in the new millennium. Large organic molecules' NLO characteristics have garnered a lot of attention over the last 20 years, prompting in-depth theoretical and experimental investigation. The second-harmonic frequency's crucial role in photonics and optoelectronics is the primary reason for this focus [1]. NLO materials find widespread application across various fields, including High-Density Optical Memories, Telecommunications, Electro-Optic Modulators, Color Displays and Optical Bistability, among others [2]. Organic NLO crystal has heightened scope due to their extraordinary optical susceptibilities [3]. In our previous reports, we have detailed the growth methodology of 1-Carboxy-2-Methylpropan-1-Aminium Chloride 2-Azaniumyl-3-methylbutanoate (CMAAM) single crystal, along with comprehensive characterizations FT-IR, FT-Raman, Z-scan study coupled with DFT analysis (B3LYP/6-311++G (d, p)) [4]. A notable example of this research is the synthesised CMAAM, which, owing to its impressive optical and structural properties, holds

substantial potentiality for applications in signal processing, optoelectronics and laser technologies. In this study, we present new insights, including the estimation of the absorption band tail of the CMAAM and the calculation of optical constants and parameters, including the Urbach energy, steepness parameter, extinction coefficient, refractive index and optical conductivity for the title material. Additionally, we investigate electronic polarizability and photoluminescence properties to provide a comprehensive understanding of the optical behaviour of the title compound, thereby making a significant contribution to the field for the very first time.

## II. EXPERIMENTAL PROCEDURE

Slow evaporation solution growth method was utilised to grow an organic single crystal of the compound 1-carboxy-2-methylpropan-1-aminium chloride 2-azaniumyl-3-methylbutanoate at 35°C temperature. Ethanol served as the solvent for a 2:1 ratio of L-Valine methyl ester (Sigma-Aldrich, 99%) and hydrochloric acid (SRL), which acted as precursor for the effective synthesis of desired material CMAAM. The chemical response can be represented as follows:  
 $2(C_6H_{13}NO_2) + HCl \rightarrow C_{10}H_{22}ClN_2O_4$

A saturated solution was generated by adding ethanol as the solvent to a stirred mixture maintained at 35°C temperature for 6 hours. It was filtered in glass beaker using a 4 µm Whatman filter paper, covered with a perforated polythene sheet and kept in undisturbed place. The slow solvent evaporation under controlled conditions facilitated nucleation, leading to crystal growth at the bottom of the beaker after several days. Over a 35-days, a single crystal measuring 4 × 1 × 1 mm<sup>3</sup> of the title compound was obtained from the solution. Fig. 1 shows the photograph of harvested CMAAM transparent organic single crystal.

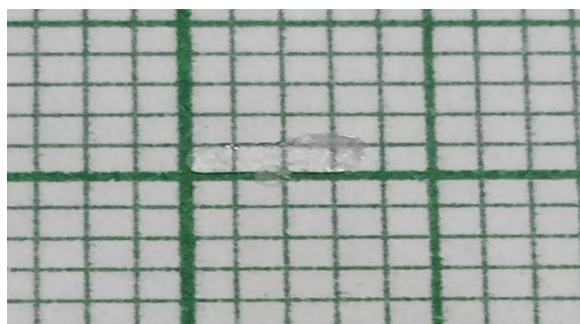


Fig. 1. Photograph of a grown crystal CMAAM

## III. EXPERIMENTAL RESULTS

### 3.1. Single-crystal X-ray diffraction analysis

X-ray diffraction analysis of the grown compound was performed to better understand its structural properties. The crystal lattice parameters of title material were identified by using a Bruker Kappa single-crystal X-ray diffractometer. Table .1 displays the title material crystallographic data. Under CCDC number 2286166, the CMAAM crystallographic information file has been deposited.

Table .1. Crystallographic detail of CMAAM single crystal

Molecular Formula	C <sub>10</sub> H <sub>22</sub> ClN <sub>2</sub> O <sub>4</sub>
Unit cell parameters	a = 11.1476(19) Å, b = 5.1724(9) Å, c = 13.030(2) Å α = γ = 90 °, β = 111.913(1) °
Crystal System	Monoclinic
Space group	P2 <sub>1</sub>
Cell volume	697.0(2) Å <sup>3</sup>
Formula weight	269.74
Z	2
Density (calculated)	1.285 Mg/m <sup>3</sup>

### 3.2. Optical studies

UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda 35) records the UV-Vis-NIR spectrum. For optical analysis, a transparent title crystal with a sample thickness of about 1 mm was examined in the range of 200–1400 nm. It was shown in Fig. 2, demonstrating commendable transparency across the entire visible spectrum and 359 nm was found to be the material's lower cut-off wavelength. The dependence of the optical absorption coefficient (α) on the photon energy helps to study the band structure of the material. When electromagnetic radiation is incident on a material, it is absorbed at a specific wavelength when the energy equals the material's energy band gap. Equation (1) is used to calculate the optical absorption coefficient of the CMAAM. Optical bandgap was assessed using equation (2), [5].

$$\alpha = \frac{2.3026}{t} \log \frac{1}{T} \quad (1)$$

$$\alpha h\nu = A(E_g - h\nu)^{1/2} \quad (2)$$

The CMAAM bandgap graph, is illustrated in Fig. 3. In plotted graph energy bandgap value was observed

at 2.92 eV. This value is significant because it provides insight into the material's electronic properties.

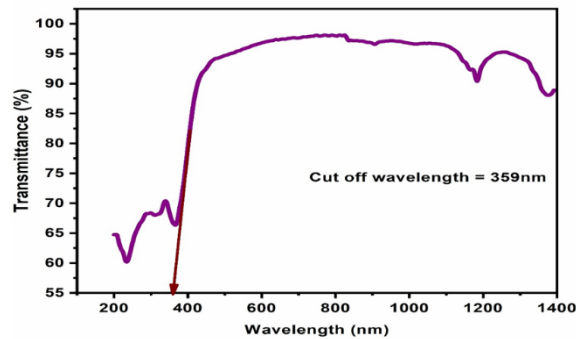


Fig. 2. UV-Vis-NIR Transmittance spectrum of CMAAM

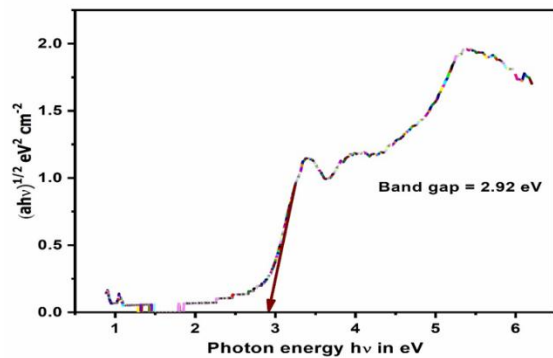


Fig. 3. Plot between  $(\alpha h\nu)^{1/2}$  and  $(h\nu)$

### 3.3. Urbach energy Estimation

Optical absorption states about the energy bandgap of the material. It plays a significant role in materials science. The optical absorption spectra of the materials can be divided into three central regions; they are the Weak absorption region, which arises from defects and impurities present in the materials, the Absorption edge region, which occurs due to perturbation of the structural disorder of the system. The area of strong absorption that determines the optical band gap energy.

Along the absorption coefficient curve, near the optical band edge, there is an exponential region called the Urbach tail.

If it is minimal, indicates a high degree of crystallinity and good perfection of lattice sites [6-8]. Urbach empirical rule, which is given by the following exponential equation (3):

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right) \quad (3)$$

where  $\alpha_0$  is a constant and  $E_U$  is Urbach energy. Logarithm on both sides of equation (3), one can get an equation of a straight line, and it is given as (4)

$$\ln(\alpha) = \ln(\alpha_0) + \left(\frac{h\nu}{E_U}\right) \quad (4)$$

Absorption band tail ( $E_U$ ) obtained from the reciprocal of the slope of the straight line obtained by plotting  $\ln(\alpha)$  vs  $h\nu$  shown in Fig. 4.

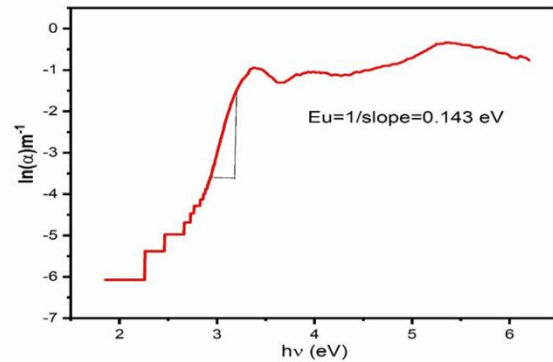


Fig. 4. Plot of  $\ln(\alpha)$  vs Photon Energy ( $h\nu$ )

From the graph the value of  $E_U$  was found to be 0.143 eV. This minimum value of  $E_U$  denotes that the grown title crystal has good crystallinity and also less disorder near the band edge. Urbach gave another relation for correlating both the optical absorption coefficient ( $\alpha$ ) and the band gap energy using relation (5),

$$\alpha = \beta \exp\left[\frac{\sigma(h\nu - E_0)}{K_B T}\right] \quad (5)$$

where  $\beta$  is a pre-exponential constant,  $\sigma$  is a steepness parameter,  $E_0$  is the transition energy, which is equal to  $E_g$  for a direct transition. But for the indirect transition, it equals to  $E_g \pm E_p$ , where  $E_p$  is the phonon energy, which is the main factor affecting the band gap energy due to thermal dissociation of lattice sites.

The CMAAM crystal has a direct band gap and hence  $E_0 = E_g$ . Taking logarithm on both sides of relation (5) it can be rewritten as  $\left(\frac{h\nu}{E_U}\right) = \left(\frac{\sigma(h\nu)}{K_B T}\right)$  (6)

Where,  $T$  is the absolute temperature (273.16 K) and  $K_B$  is the Boltzmann constant ( $8.6173 \times 10^{-5}$  eV/K). The steepness parameter represented by  $\sigma$  and it can be calculated by using equation (7)

$$\sigma = \frac{K_B T}{E_U} \quad (7)$$

The steepness parameter was determined to be 0.1646. It is utilized to relate  $E_{e-p}$ , the strength of electron-phonon interaction of the crystal [9], which is computed using the subsequent relation (8) and it was

found to be 4.0502.

$$E_{e-p} = \frac{2}{3\sigma} \quad (8)$$

### 3.4. Determination of Optical Constants

The wavelength-dependent linear refractive index (n) is key parameter for developing NLO devices such as optical parametric oscillators and electro-optic modulator. Materials with a high refractive index have many applications in creating optoelectronic devices, including organic light-emitting diodes, dispersive prisms, power lenses, and image sensors [10]. The refractive index of a compound varies with the wavelength of incident light, as well as carrier density, crystal composition, and temperature [11]. Additionally, it is essential for calculating phase-matching angles in nonlinear optical crystals [12]. The amount of light lost by scattering and per unit of absorption in a participating material is called by extinction coefficient (K) [13]. It is derived from following relation (9) The extinction coefficient of the crystal as a function of hu is shown in Fig. 5.

$$K = \frac{\alpha\lambda}{4\pi} \quad (9)$$

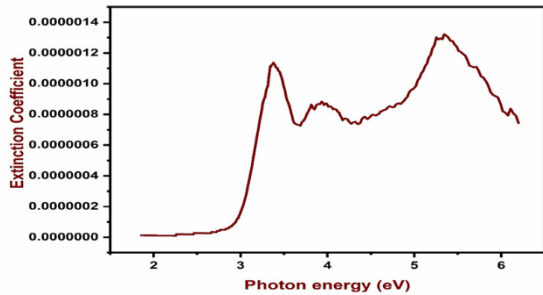


Fig. 5. Plot of Photon Energy Vs Extinction Coefficient

The refractive index from reflection data was estimated by applying the following relation (10). The graph of refractive index versus wavelength is shown in Fig. 6.

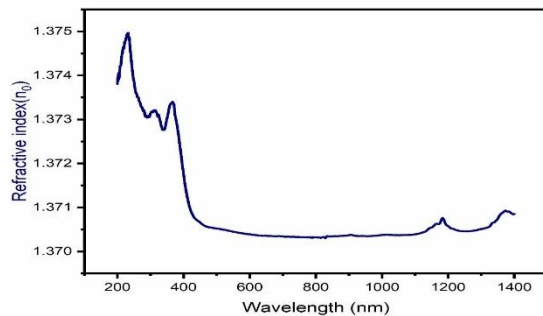


Fig. 6. Wavelength dependence of Refractive indices (n<sub>0</sub>)

From the graph linear refractive index was measured to be 1.370 at 532 nm since material has centrosymmetric nature

$$n = \frac{-(R+1) \pm \sqrt{(-3R^2+10R-3)}}{2(R-1)} \quad (10)$$

The optical conductivity ( $\sigma_{op}$ ) [14] is a measure of a grown material frequency response to light irradiation and was calculated using relation (11). CMAAM optical conductivity versus photon energy is shown in Fig. 7.

$$\sigma_{op} = \frac{\alpha n c}{4\pi} \quad (11)$$

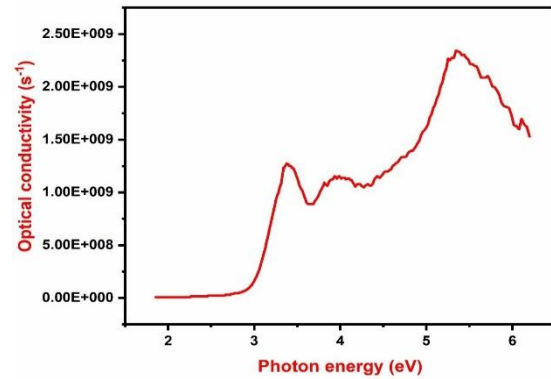


Fig. 7. Optical Conductivity as a function of Photon Energy

Fig. 7 indicates that the optical conductivity increases sharply with increasing hu for the investigated compound. It attributed to rise in the absorption coefficient. The CMAAM material exhibits high optical conductivity, confirming its very high photo response.

### 3.5. Electronic polarizability

The electronic polarizability ( $\alpha$ ) [15] of CMAAM was estimated by using Lorentz-Lorenz equation (12) and optical bandgap relation (13) and the values are given in Table .2.

$$\alpha = \frac{3M}{\pi N_{Ap}} \left[ \frac{n_0^2 - 1}{n_0^2 + 2} \right] \text{cm}^3 \quad (12)$$

$$\alpha = \left[ 1 - \frac{\sqrt{E_g}}{4.26} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{cm}^3 \quad (13)$$

Table .2. Electronic polarizabilities of the CMAAM single crystal

Electronic polarizability ( $\alpha$ )	Values of the CMAAM crystal (cm <sup>3</sup> )
Lorentz-Lorenz equation	2.5762 x 10 <sup>-23</sup>
Optical band gap	4.8139 x 10 <sup>-23</sup>

### 3.6. Photoluminescence Studies

Fig. 8 shows CMAAM photoluminescence (PL) emission spectrum. It was recorded between 350 and 650 nm using a Jobin Yvon Spex spectrofluorometer. From the figure, a broad peak was observed in the range of 450–495 nm, indicating that the grown crystals exhibit blue fluorescence and the material may have potential applications in opto-electronic devices [16]. The strong PL emission confirms its high structural perfection and this study suggests grown material applicable for fluorescent lamps, lasing media, X-ray image plates, etc. [17–19].

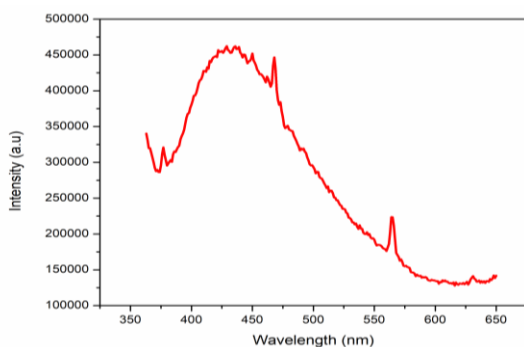


Fig. 8. Photoluminescence spectrum of CMAAM

## IV. CONCLUSION

A transparent, nonlinear optical single crystal of 1-Carboxy-2-Methylpropan-1-Aminium Chloride 2-Azaniumyl-3-methylbutanoate was carefully grown by slow evaporation solution growth method at 35°C temperature. XRD analysis revealed crystal's space group and confirmed that CMAAM was a member of the monoclinic crystallographic system. In-depth UV-Vis-NIR studies showed a notable optical cut-off wavelength at 359 nm, and energy bandgap of 2.92 eV of the grown compound. Minimal Urbach energy shows the excellent crystalline quality of the title compound, with fewer defects and a highly ordered atomic arrangement. Refractive index, the extinction coefficient, and optical conductivity graphs for the title compound were plotted as the function of optical absorption, wavelength and photon energy. CMAAM electronic polarizability was calculated based on optical band gap energy relation and Lorentz-Lorenz equation. Photoluminescence studies revealed that the material's blue fluorescence was appropriate for the fabrication of photonic devices.

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### Author contributions

N Mahalakshmi: Methodology, Conceptualisation, Data curation and Writing-original draft, Validation, Formal analysis. M.Parthasarathy: Writing- review & editing, Validation, Formal analysis.

### Declarations

Ethical approval and consent to participate All experiments were carried out by following the university guidelines. None of the authors used human beings as research subjects.

Consent to publish In the present study, there were no person's data in any form

### Conflict of interest

There is no conflict of interest between the author and the co-author in bringing out the publication of this work in this journal.

### Data availability statement

The data presented in this study are available upon request from the corresponding author.

### Funding Declaration Statement

The authors did not receive support from any organization for the submitted work.

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