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Spectral, Optical and Thermal Characterization of 2-Aminothiazolium 4-Chlorobenzoate Single Crystal

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Abstract
2-Aminothiazolium 4-Chlorobenzoate (2AT4CB) crystals have been grown by slow evaporation method. The crystal has been characterized by FTIR, UV-Vis NIR Spectrum, Thermogravimetric analysis and Photoluminescence for its suitability for optoelectronic applications. In the UV Vis NIR spectrum the cut-off wavelength is observed at 380 nm with the energy band gap of 3.4 eV. In the photoluminescence spectrum, the emission wavelength is observed at 362 nm with the energy band gap value of 3.42eV. The various optical constants such as refractive index, reflectance, absorption coefficient, extinction coefficient, optical conductivity, electrical conductivity and susceptibility of the material has been determined for its suitability of optoelectronic applications.
Keywords: *transmittance,optical constants, emission, decomposition*

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I. INTRODUCTION

Optical characterization of a material is indispensable to understand the suitability of the material for optical applications. Numerous researches have been going on for more than a decade to search novel organic crystals for optical applications. The organic crystals show promising results than inorganic crystals as its many applications in optical communication, information storage and optical switching have been reported [1-3]. The chemical structure of the organic material can be tuned to get the desired optical effect [4]. The study of the various parameters of the crystal such as absorption, transmittance, reflectance, refractive index, extinction coefficient, thermal stability optical conductivity, electrical conductivity and photoluminescence are essential to examine the material's suitability for optoelectronic applications [5]. Even though 2-aminothiazole possesses excellent applications in the field of medicines, very few studies were carried out regarding the optical properties.2-aminothiazolium 3,5 dinitrobenzoic acid complex and 2-aminothiazole-3,5-dinitrosalicylic acid complex have been reported[6, 7]. The identification of structural and spectral features of 2-amino 4-chlorobenzoic acid and 4-amino 2-chlorobenzoic acid has been reported [8]. In this work, the 2-aminothiazole molecule is protonated through hydrogen transfer from the carboxylic group of the 4-chlorobenzoic acid. The crystal structure and optical characterization of 2-aminothiazolium 4-flouro benzoate (2AT4FB) has been reported earlier in the M.Phil. Thesis [9, 10]. Aroused by the curiosity of the optical properties of 2AT4CB, we have grown the crystals of 2-aminothiazolium 4-chlorobenzoate (2AT4CB) and the crystal have been characterized by FTIR, UV-Vis NIR, thermal and photoluminescence for its suitability as optical material for optoelectronic applications. The various optical values such as band gap, refractive index, reflectance, absorption coefficient, extinction coefficient, excitation wavelength, thermal stability, optical conductivity and electrical conductivity of the crystal has been determined. Fig. 1.shows the grown crystal.The chemical diagram of the grown crystal is shown in Fig. 2.

1.1 Experimental

2-Aminothiazole (Otto) and 4-Chlorobenzoic acid (Avra synthesis) were dissolved in ethanol in the molar ratio of 1:1.The two solutions were allowed to react together at the room temperature with continuous stirring. Clear brown solution obtained was allowed to evaporate slowly. Brown colour crystals were harvested after fifteen days.

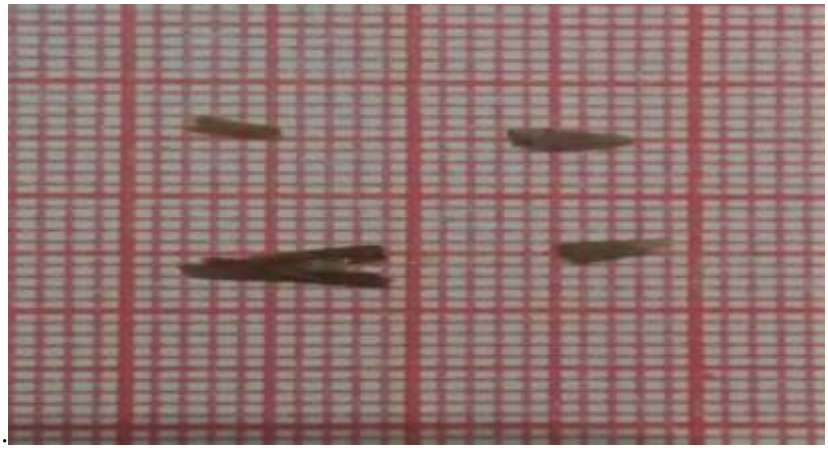

Figure1.Crystals of 2AT4CB

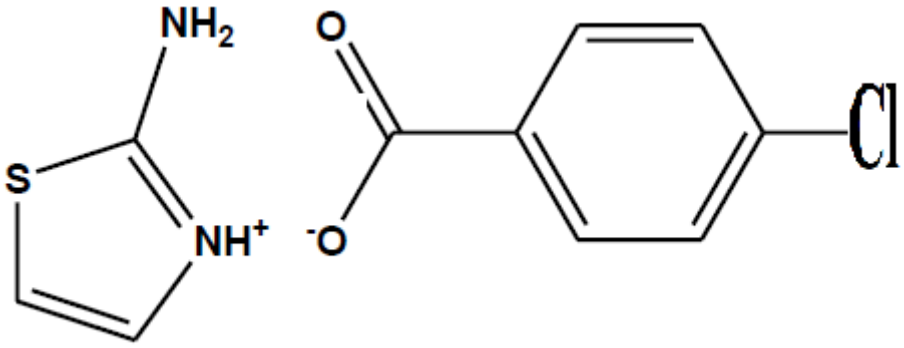

Figure2. Chemical diagram of 2-Aminothiazolium 4-Chlorobenzoate

II. RESULT AND DISCUSSION

2.1 Fourier transform infrared (FT-IR) analysis

Fourier transform infrared spectrum of 2-AT4CB single crystal was recorded in Perkin-Elmer Spectrometer in the range of 4000 cm^{-1} to 400 cm^{-1}using KBr pellet technique. The purpose of the FTIR study is to confirm the presence of functional groups and intermolecular hydrogen bonding. The bonded O-H group generally gives rise to a broader band than the N-H group. In the spectrum of the 2-AT4CB, the broad band observed in the region 3451 cm^{-1} is due to O-H stretching and its involvement in intermolecular hydrogen bonding, confirms the presence of –OH and –NH in the crystal [11]. The peaks at 2919 $cm^{-1}$and 2850cm^{-1} is due to the C-H symmetric stretching vibration. The C=O vibration peak of COO^- in 4-chlorobenzoate is observed at 1624 cm^{-1}. In the free 4-chlorobenzoic acid the C=O vibration occurs at 1685 cm^{-1}.The shift towards low value indicates the transfer of carboxylic proton from carboxylic acid to 2-aminothiazole [11]. The band at 1464 cm^{-1} is assigned to the aromatic C=C stretching vibrations. A band at 1399 cm^{-1} is assigned to the C-O stretching vibration. The bands at 1082 cm^{-1} is assigned to C-N stretching vibration. The band at 720 cm^{-1} is due to the C-Cl stretching [8]. The FT-IR spectrum of 2AT4CB is shown in Fig. 3.Table 1. Shows the wave number with assigned frequencies.

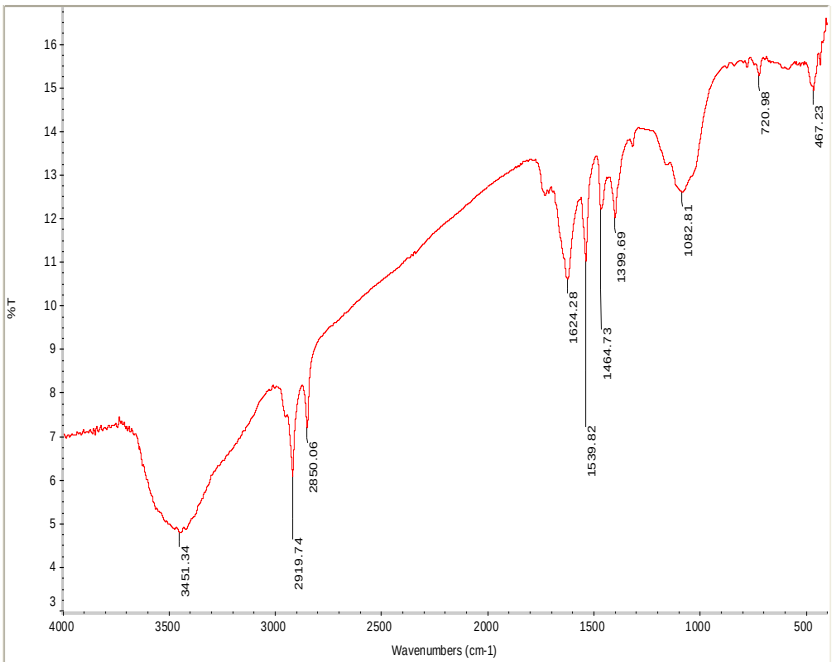

Figure 3. FTIR Spectrum of 2AT4CBA

S. No.	Wavenumber (cm^{-1})	Bond
1	3451.34cm^{-1}	O-H intermolecular hydrogen bonding
2	2919.74cm^{-1}	C-H stretching
3	1624.28cm^{-1}	C=O stretching
4	1539 cm^{-1}	COO^- asymmetric stretching
5	1464 cm^{-1}	C=C stretching
5	1399 cm^{-1}	C-O stretching
6	1082cm^{-1}	C-N stretching
7	720.98 cm^{-1}	C-H bending
8	467 cm^{-1}	C-Cl stretching

Table1.Wavenumber with assigned frequencies

2.2 Optical Studies of 2AT4CB

2.2.1 UV Vis NIR Study

Since single crystal is mainly used in optical applications, the optical transmission range and the frequency of cut off wavelength are important. The optical absorption plays an important role in identifying the potential of the NLO material.The UV-Vis-NIR absorption spectrum of the grown crystal was recorded in the wavelength range of 190-1100 nm shown in Fig. 4. The recorded transmission spectrum is shown in Fig. 5. The cut-off wavelength is 380 nm. The material shows very good transmittance over the entire visible range from 400 nm to 1100nm and it has 98% transparency. The poor absorption in the range of 400 nm to 1100 nm indicates that the material can be used for optoelectronic applications [12].

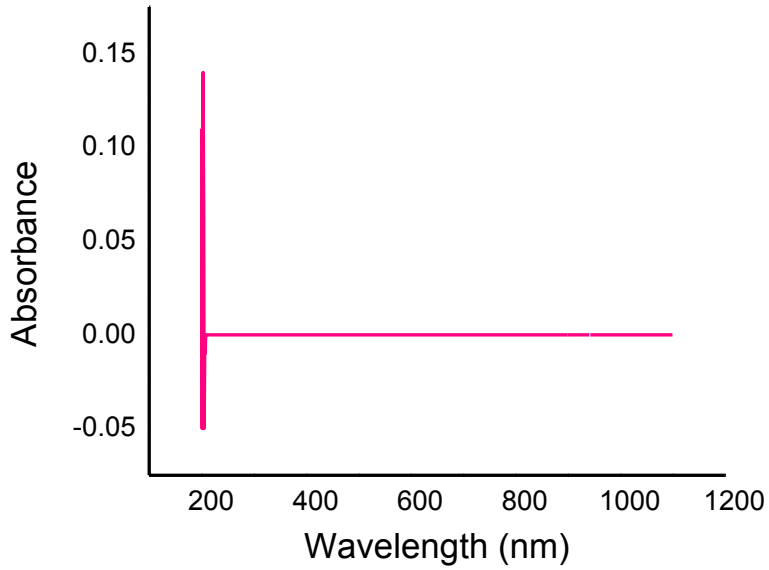

Figure4. UV absorbance of 2AT4CB

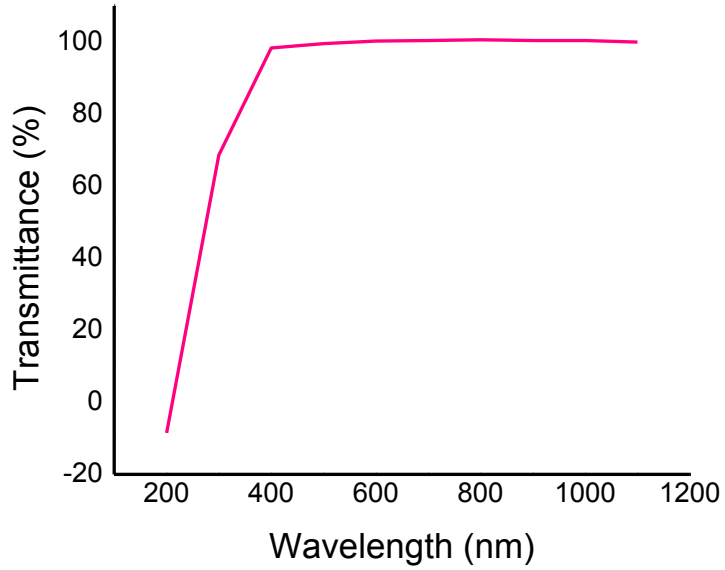

Figure5. UV transmittance of 2AT4CB

2.3 Determination of optical constants

The optical properties of a crystal can be derived mainly from its optical transparency, band gap, extinction coefficient, reflectance, refractive index, optical conductivity and electrical conductivity. The optical properties of crystals are governed by the interaction between the crystal and the electric and magnetic fields of the electromagnetic wave.

2.3.1 Optical Band Gap

As the material absorbs the photon of incident light, an electron is excited from lower to upper energy level or state. This transition of electron can be direct or indirect. In a direct transition an electron in the conduction band can fall to an empty state in the valence band, giving off the energy difference E_g as photon of light. On the other hand, if an electron in the conduction band cannot fall directly to the valence band, but must undergo a momentum change as well as changing its energy. The difference between direct and indirect band structure is very important for deciding that which semiconductor can be used in device requiring light output [13].

The optical absorption coefficient (α) is the fraction of incident energy intensity decreased per unit distance in an absorbing medium was calculated from the transmittance.
The optical absorption coefficient (α) was calculated using equation.

$$\alpha = \left(\frac{2.3036}{t}\right) log \frac{1}{T} m^{-1}$$

Where T is the transmittance and t is the thickness of the crystal.
The optical band gap energy (E_g) is related to absorption coefficient (α) and photon energy (hυ) through the Tauc relation [13]

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

Where A is optical constant, E_g is the optical band gap energy, h is the Planck's constant and υ is the frequency of the incident photon. The band gap of grown 2AT4CB crystal was computed by plotting $(\alpha h\upsilon)^2$versus hυand it is shown in the Fig. 6. From the Tauc's plot the optical band gap is observed as 3.4 eV.

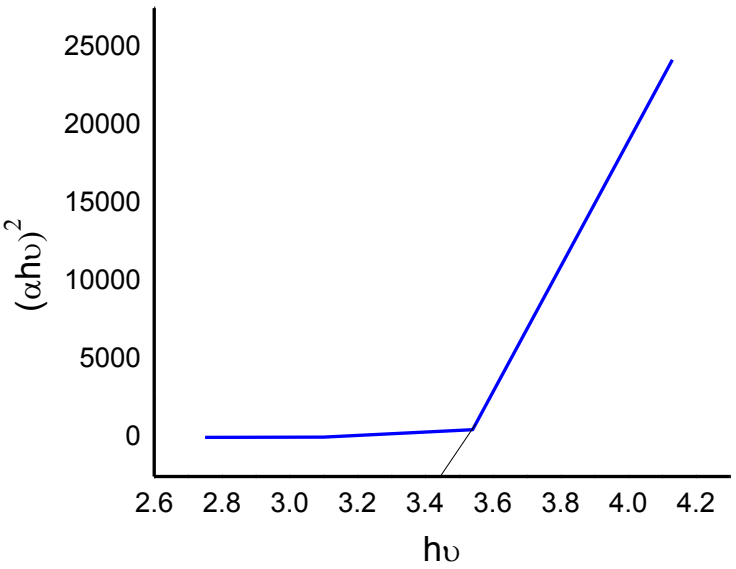

Figure6. Plot of hυ versus $(\alpha h\upsilon)^2$

2.3.2 Optical constant

The optical constants (n, k) were determined from the transmission (T) and reflection (R) spectrum based on the following relations [14].

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)}$$

Where t is the thickness and R is the reflectance.
Extinction coefficient (k) is the fraction of light loss due to scattering and absorption per unit distance in a participating medium.
The extinction coefficient K can be calculated using the below relation

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

Where α is the optical absorption coefficient, λ is the wavelength. The plot of extinction coefficient Vs wavelength is shown in Fig. 7.

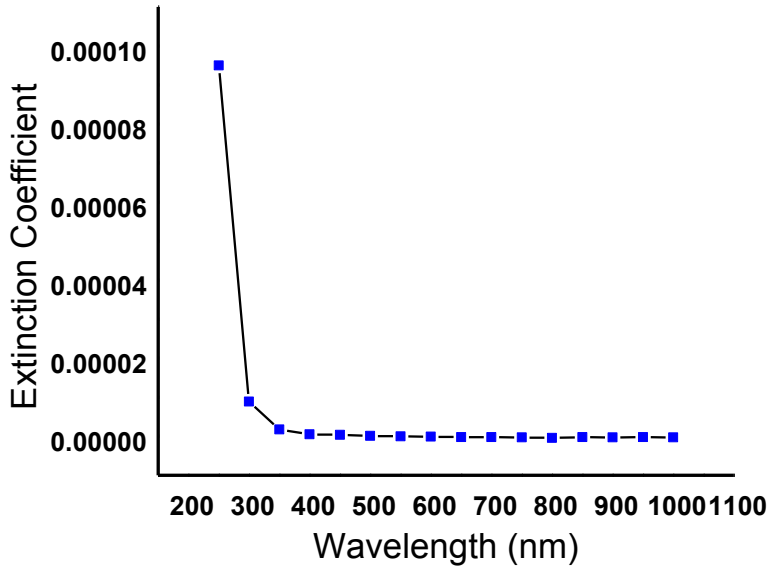

Figure7. Plot of wavelength versus extinction coefficient of 2AT4CB

The reflectance R gives the ratio of the energy of reflected to incident light from the crystal.The reflectance (R) in terms of absorption coefficient (α) and the thickness of the crystal (t) can be determined using the below relation

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

Reflectance as a function of wavelength is graphically illustrated in Fig. 8

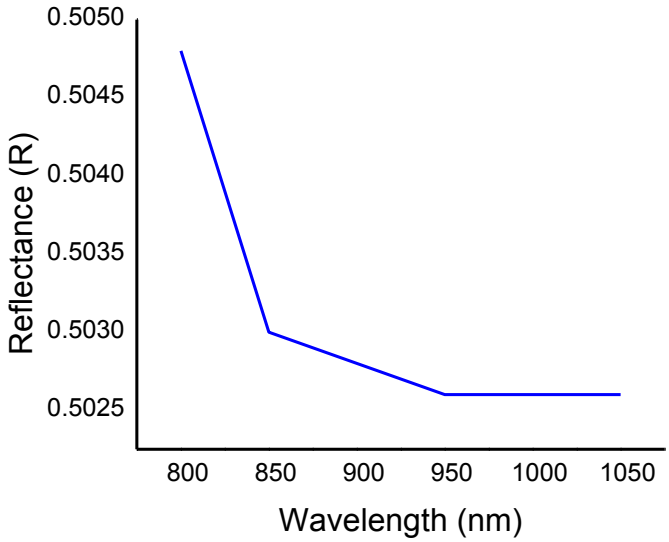

Figure8. Plot of wavelength versus reflectance of 2AT4CB

Generally refractive index of a substance is a measure of the speed of light in that substance (n=c/v), is the key parameter for optical device design.

Refractive index (n) can be determined from reflectance data using the equation [15],

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

The calculated refractive index (n) value using the above equations for the grown 2AT4CB is 2.59. The plot of wavelength versus refractive index is shown in Fig. 9.

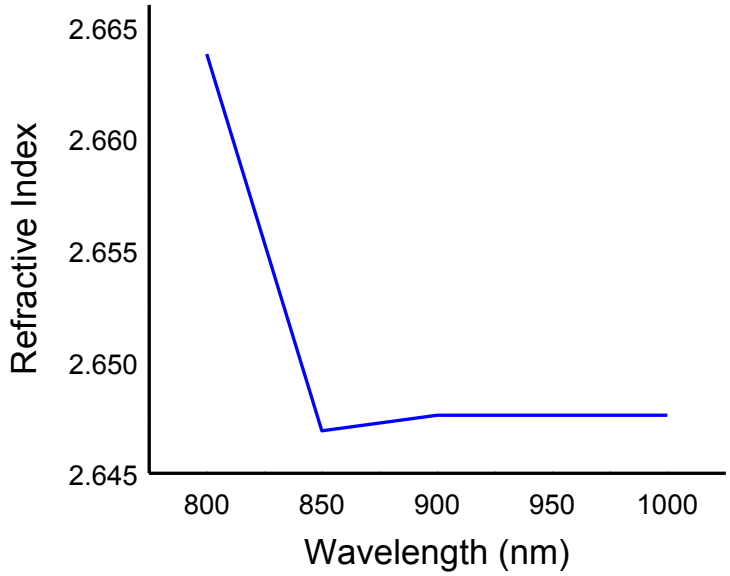

Figure9. Plot of wavelength versus refractive index of 2AT4CB

Optical Parameter	2-Aminothiazolium 4-Chlorobenzoate
Cut-off wavelength	380 nm
Optical energy bang gap (E_g)	3.4 eV
Refractive index (n)	2.59
Extinction coefficient	0.000006233
Reflectance	0.5033
Optical conductivity	0.19616
Electrical Susceptibility	0.5242

Table2. Optical data of 2AT4CB single crystal

2.3.3 Optical Conductivity

The optical response of a material is studied in terms of the optical conductivity. Optical conductivity is one of the powerful tools for studying the electronic states in materials. It has dimensions of frequency which are valid only in a Gaussian system of units. The optical conductivity (σ_{op}) has been determined from the relation

$$\sigma_{op}=\alpha nc/4\pi$$

Where c is the velocity of light, α is the optical absorption coefficient and n is the refractive index. The variation of optical conductivity with wavelength is shown in Fig. 10. Optical conductivity has higher values in the UV region of the order of $1*10^8 S^{-1}$

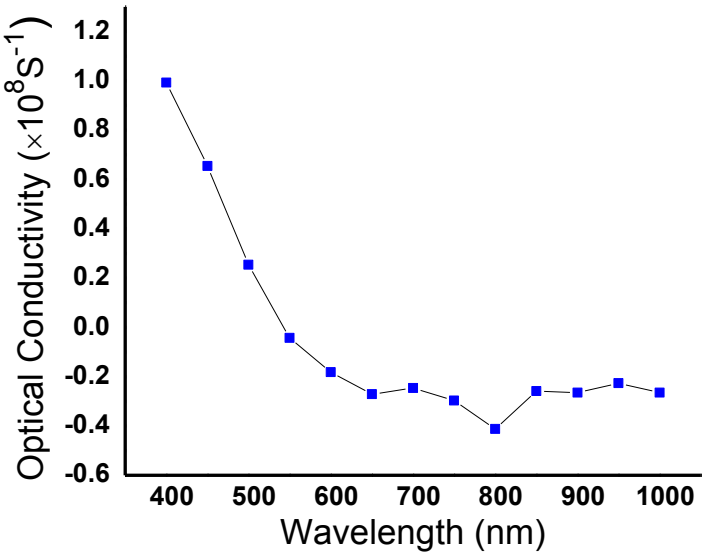

Figure10. Plot of wavelength versus optical conductivity of 2AT4CB

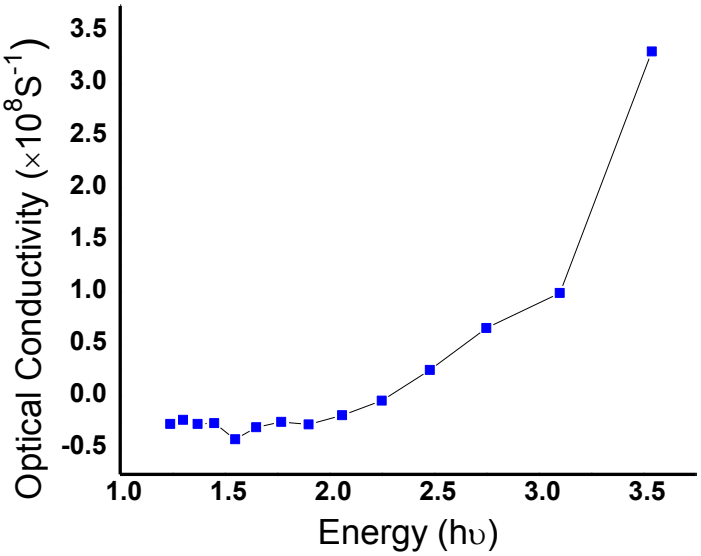

Figure11. Plot of energy versus optical conductivity of 2AT4CB

The optical conductivity of 2AT4CB increases with increase in photon energy in the Fig. 11 indicates the very good optical response of the material. The higher value of optical conductivity (10^{9}-10^{12}) shows very good photo response of the crystals [16]. Here in our case the optical conductivity is higher in the order of $10^{8}S^{-1}$. It indicates that 2AT4CB exhibits almost very good optical response.

2.3.4 Electrical Conductivity

The value of electrical conductivity of a materialis related with the optical conductivity value of the crystal using the following equation

$$\sigma_e = 2\lambda\sigma_{op}/\alpha$$

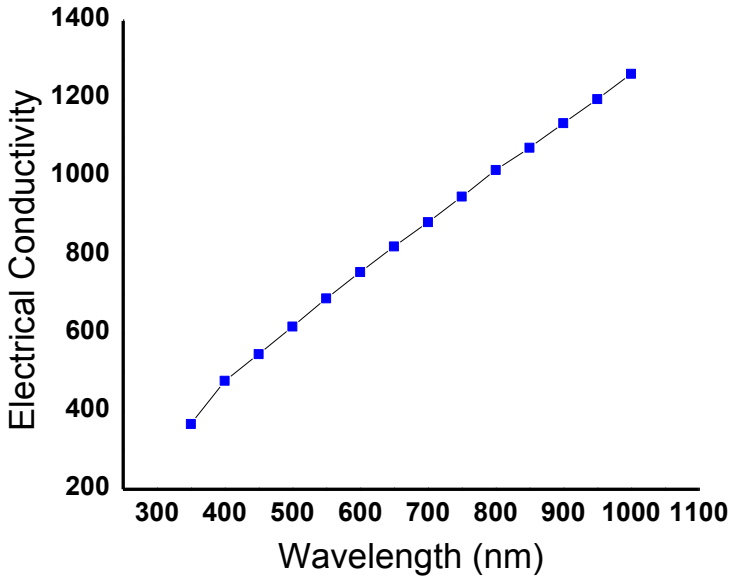

Figure12. Wavelength versus electrical conductivity of 2AT4CB

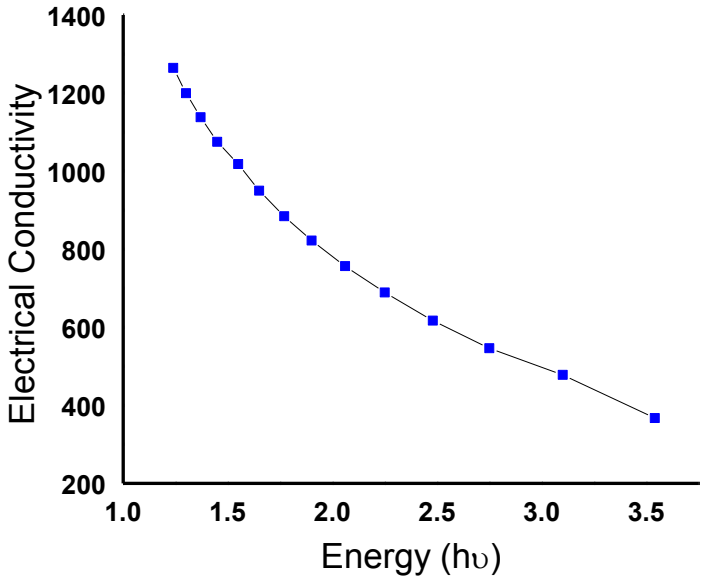

Figure13. Plot of energy versus electrical conductivity of 2AT4CB

2.3.5 Electric Susceptibility

The electric susceptibility (χ_c) can be calculated from the following relation [17, 18].

$$\varepsilon_r=\varepsilon_0 + 4\pi\chi_c=\eta^2 - k^2$$

$$\chi_c = \eta^2 - k^2 - \varepsilon_0/4\pi$$

Where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The complex dielectric constant is given by ε_c. The real and imaginary part of dielectric constant from extinction coefficient are given as [18-20].

$$\varepsilon_c = \varepsilon_r + \varepsilon_i$$

$$\varepsilon_r = n^2 - k^2$$

$$\varepsilon_i = 2nk$$

Where $\varepsilon_r$and ε_i are real and imaginary part of dielectric constant.

The electric susceptibility is calculated as $\chi_c = 0.5242$. The real ε_r and imaginary ε_i values of dielectric constant are 6.7184 and $3.229*10^{-5}$.

2.4 Photoluminescence

Photoluminescence is one of the effective tools to provide relatively direct information about the physical properties of the materials at the molecular level, including shallow and deep level defects and band gap states [21]. The photoluminescence spectrum was recorded for the 2AT4CB crystal in the range of 300-600 nm with excitation wavelength of 350nm at room temperature is as shown in Fig. 14. The band gap energy is calculated using the formula,

$$E_g = \frac{1240}{\lambda}$$

Two strong intense emission peaks observed at 362 nm (E_g=3.42 eV) and 596 nm (E_g= 2.0 eV) respectively. This indicates the bluish fluorescence and yellow fluorescence emission. This result indicates that the 2AT4CB have a UV and visible emission and the crystals might be suitable for UV filters and optoelectronic laser devices.

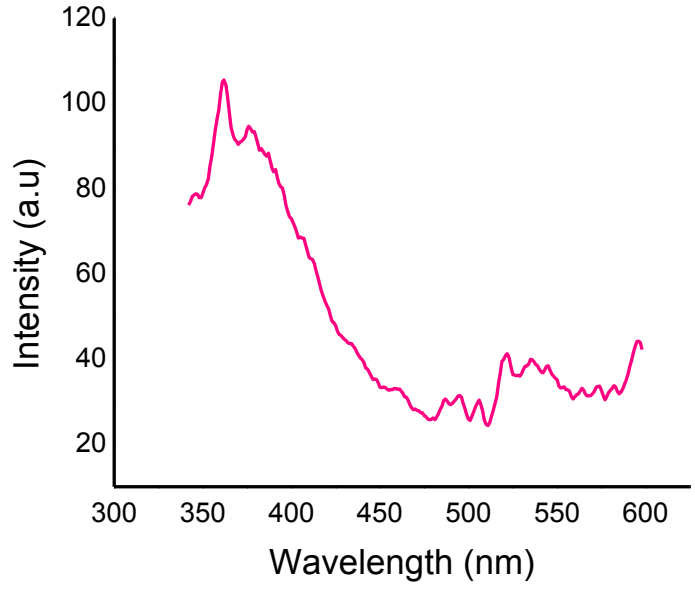

Figure14. Excitation Spectrum of 2AT4CB

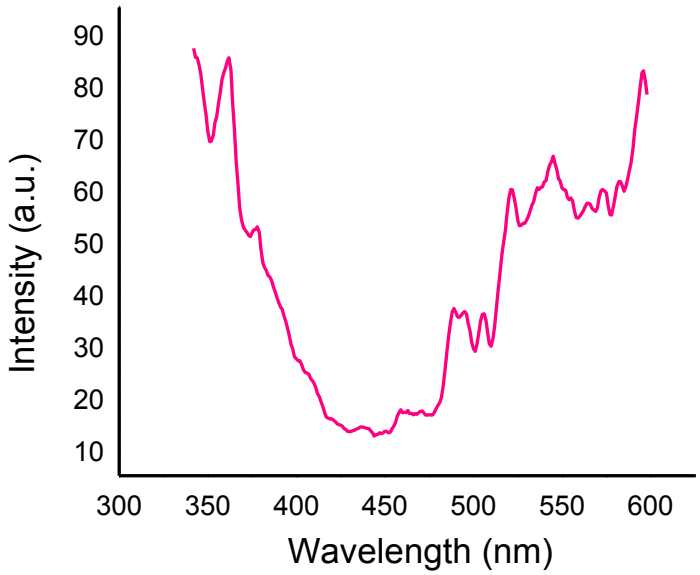

Figure15. Emission Spectrum of 2AT4CB

2.5 Thermogravimetric TGA/ DSC analysis

Thermal analysis is used to find out the weight loss (TGA) and (DSC) thermal stability of the grown crystal with respect to the temperature. The TGA curve gives the quantitative measurement of mass change associated with the transition [22]. TGA was carried out on the crushed specimen of 2AT4CB crystal by employing TGA analysis at 10°c/min heating rate in the nitrogen atmosphere shown in fig. 16. In DSC analysis, the endothermic peak at 135°cis attributed to the melting point of the crystal. There is no phase transition till the material melts and thus indicates the utility of the crystal for NLO applications. The absence of water of crystallization in the molecular structure is confirmed by the absence of weight loss at 100°c. The weak endothermic peak at 220°c indicates the decomposition of the compound. From the TGA curve it is found that the first stage of decomposition of the grown crystal starts at 130°c. Further decomposition is observed from 250°c and reaches 10% residue. It is concluded that the crystal is thermally stable upto 130°c. Almost 80% of the starting material is lost around 250°c. Further, the crystal is completely decomposed around 680°c.

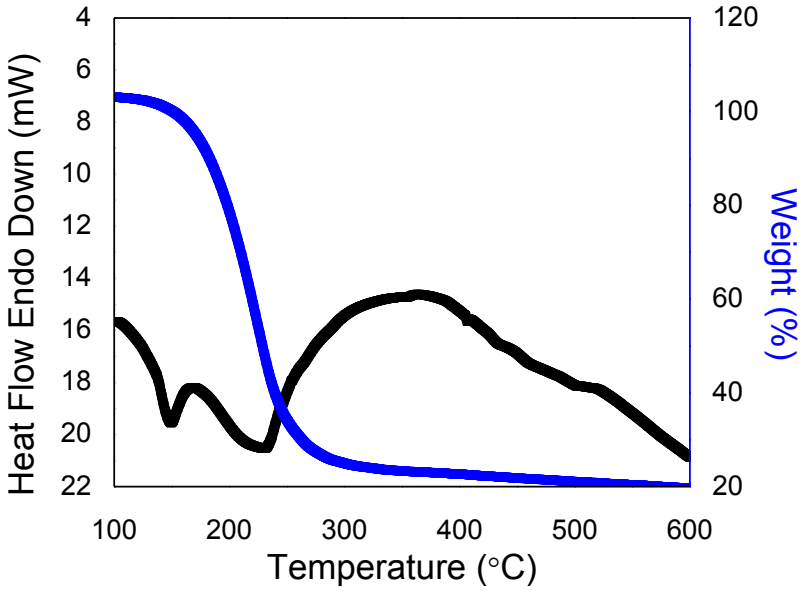

Figure 16. TGA/DSC of 2AT4CB

III. CONCLUSION

Single crystal of 2AT4CB was grown by slow evaporation method at room temperature. Brown transparent crystals were obtained after fifteen days. Fourier Infrared Spectroscopic studies were carried out to identify the different vibrations and the functional groups. The UV-Vis NIR absorption or transmittance shows a lower cut-off wavelength of 380 nm. From the thermal studies, the stability of the crystal is observed to be up to 131.4 °c and there is no structural phase transition in the low temperature region. The lower cut-off wavelength of 380 nm indicates the suitability of the title compound suitable for NLO applications in the entire visible region and the near infrared region.The electric susceptibility is calculated as χ_c = 0.5242. The real ε_r and imaginary ε_i values of dielectric constant are 6.7184 and $3.229*10^{-5}$. Optical conductivity has higher values in the UV region of the order of $1*10^{8}S^{-1.}$ The optical conductivity of 2AT4CB increases with increase in photon energy indicates the very good optical response of the material. From this various optical studies and the results, we conclude that the material 2AT4CB is suitable for optoelectronic applications.

REFERENCES

[1]. Kaino, T., Cai, B. andTakayama, K., "Fabrication of DAST channel optical, waveguides", Advanced functional materials, Vol.12, no 9, pp.599-603, 2002.
[2]. Prasad, P.N. and Williams, D.J., Introduction to Nonlinear Optical effects in Molecules and Polymers, John Wiley and sons, New York, NY, USA, 1991.
[3]. Periyasamy, B.K., Jebas, S.R. andThailampillai, B., "Synthesis and Spectralstudies of 2-aminopyridinium para-nitrobenzoate: a novel optoelectronic crystal. Material Letters, vol 61, no.7, pp. 1489-1491, 2007.
[4]. RW. Munn, CN. Ironside, Priciples and applications of nonlinear optical materials, London, 1993.
[5]. Dongol, M., "Optical absorption and structural properties of as deposited and thermally annealed As.Te.Ga thin films", Egyptian Journal of Solids, vol. 25 no 1, pp.33-47, 2002.
[6]. Devendhiran, T., Kumarasamy, K., Ching, M.and Lin. Frontiers in Advanced Materials Research, 42-45 2019.
[7]. Chandrasekaran, J., Babu, B., Balaprabhakaran, Ilayabarathi, P.and Maadeswaran, P. Optoelectronics and Advanced Materials-Rapid Communications, Vol. 6, No.1-2, January-February 2012, p.211-213.

[8]. Kaya Kinayturk, N.,Oturak, H., Special Issue of the 2 nd International Conference on Computational and Experimental Science and Engineering, 2015. DPI: 10.12693/APhysPolA.130.276.
[9]. Keerthana, A., "Spectral Characterization and Single Crystal X-Ray Diffraction Studies of 2-aminothiazolium 4-fluorobenzoate", M.Phil Thesis, April – 2020, Department of Physics, KamarajarGovernment Arts College, ManonmaniamSundaranar University.
[10]. Dhana Lakshmi, S., "Optical Characterization of 2-Aminothiazole and 2-aminothiazolium 4-fluorobenzoate single Crystal", M.Phil Thesis, April – 2021 Department of Physics, KamarajarGovernment Arts College, ManonmaniamSundaranar University.
[11]. Kumeresan, S., Seethalakshmi, P.G., Kumaradas, P.and Devipriya, B. Synthesis and structural characterization of organic co-crystals. Journal of Molecular structure, 1032 (2013) 169-175.
[12]. Divya, R., Lekshmi, P.N., Bijini, B.R., Nair, C.M.K., Gopakumar, N., RajendraBabu, K., A novel structure of gel grown strontium cyanurate crystal and its structural, optical, electrical characterization, Physica*B* Condens.Matter, 526, **2017**, 37-44.
[13]. Tauc, J., Grigorovici, R., Vancu, A. Optical Properties and electronic structure of amorphous Germanium. Phys. Status Solidi B, 1996, 15, 627-637.
[14]. M. Dongol, "Optical absorption and structural properties of as deposited and thermally annealed As-Te-Ga thin films", Egyptian Journal of Solids, Vol.25, no.1, pp. 33-47, 2002.
[15]. Ashour, A., EI-Kadry, N. and Mahmoud, S.A., "On the electrical and optical properties of CdS films thermally deposited by a modified source", Thin Solid films., vol. 269, no.1-2,pp.1555-162,2000.
[16]. HiralRaval, B.B., Parekh, K.D., Parikh and M.J. Joshi. Growth and characterizations of organic NLO Imidazolium L-Tartrate (IMLT) single Crystal. Hindawi, Advances in condensed matter physics, Volume 2019, Article ID 3853215, 9 pages.
[17]. Urbach, F., "The long wave length edge of photographic sensitivity and of the electronic absorption of solids", Physical Review A: Atomic, Molecular and Optical Physics, vol. 92, no. 5, pp. 1324-1325, 1953.
[18]. Gupta, V. and Mansingh, A., "Influence of postdeposition annealing on the structural and optical properties of sputtered zinc oxide film."Journal of Applied Physics, vol. 80, no. 2, pp.1063-1073, 1996.
[19]. Kochuparampil, A.P., Joshi, J.H. and Joshi, M.J., "Growth , structural, spectroscopic, thermal, dielectric and optical study of cobalt sulphide-doped ADP crystals", Modern Physics Letters B, vol.27, Article ID 1750246, 2017.
[20]. Dhanaraj, P., Suthan, T. and Rajesh, N., "Synthesis, crystal growth and characterization of semi organic material: calcium dibromide bis (glycine) tetrahydrate", Current applied physics, vol.10, no. 5, pp.1349-1353, 2010.
[21]. DivyaBharathi, M., Ahila, G., Mohana, G., Bhuvaneswari, R and Anbalagan, G. Materials Science and Engineering 360 (2018) 012057.
[22]. Karpagam, T and Balasubramanian, K. Comparative study of mechanical, Dielectric and Thermal properties of Solution Grown NLO Crystal Potassium Acid Pthalate doped with L-Phenylalanine and L-Tryptophan. IJSRSET 1844157, Volume 4/ Issue 4/ March/April 2018 [(4)4: 731-737.