

**SYNTHESIS, GROWTH AND CHARACTERIZATION OF
2-AMINO 6-METHYLPYRIDINIUM 6-AMINOCAPROATE
NONLINEAR OPTICAL SINGLE CRYSTAL**S. Muniyasamy^a, G. Rajasekar^b, P. Iswarya^a, M. Muneeswari, M. Vallikkodi, S. Sudhahar *^a Department of Physics, Alagappa University, Karaikudi-630003, India.^b Department of Physics, Presidency College, Chennai-600005, India.

ABSTRACT - New nonlinear optical single crystal of 2-Amino-6-methylpyridinium 6-Aminocaproate (2A6M6A) was grown by slow evaporation method using water as a solvent. The grown 2A6M6A crystal was characterized and confirmed by Single crystal X-ray diffraction. It is a monoclinic structure with noncentrosymmetric space group P. The lattice parameters of the grown crystal is found to be $a = 8.54 \text{ \AA}$, $b = 5.89 \text{ \AA}$, $c = 15.24 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 102.86^\circ$ and volume $V = 748 \text{ \AA}^3$. The crystalline perfection was confirmed by Powder X-Ray diffraction analysis. The grown 2A6M6A functional groups and chemical composition were confirmed by the FT-IR and Laser Raman spectroscopy analysis. Optical studies are important criteria for the optical applications. The grown crystal was subjected to the UV analysis, from the figure it is observed that the cut off wavelength at 295 nm and there is no absorption in the entire visible region. The band gap of the grown 2A6M6A crystal is found to be 4.13 eV. The photoluminescence spectra give the qualitative and quantitative analyses of 2A6M6A grown crystal. The excitation wavelength at 386 nm and the high intensity peak was observed at 460 nm. Thermal stability of the material is confirmed by the thermal analysis; it is stable upto 193 °C. Nonlinear optical studies confirmed by the Kurtz-Perry powder SHG test. The grown 2A6M6A crystal is 2.6 times higher than that of KDP Crystal.

KEYWORDS: Growth from solution; Organic compounds; Optical properties; Thermal property; NLO Test.

I. INTRODUCTION

Designing a crystal structure with noncentrosymmetric packing intensely facilitates their use in various fields such as ferroelectricity, piezoelectricity, pyroelectricity and second order nonlinear optics (NLO) [1-4]. An assortment of strategies has been put forward towards the development of new materials with noncentrosymmetric packing [5]. As a consequence many organic NLO materials have been fabricated which has potential applications such as fast response time, high non-linear response, wide transparency range, high electronic susceptibility ($\chi^{(2)}$) and facile modification which exploit them as a suitable candidate for optoelectronics and photonics industries [6-9]. The materials, which can be produce green/blue laser light and withstand at high-energy light radiation, are of great importance for future technology. The organic compound of Aminocaproic acid is an Antifibrinolytic Agent. It is very useful to produce size and shape controlled particles including their organized self-assembled nanostructures. It consists of COOH proton donor group. One of the 6-Aminocaproic acid derivative crystals is an analogue of lysine, which makes it an effective inhibitor of plasminogen, a proteolytic enzyme. Pyridine heterocycles and their derivatives are present in many large molecules having photo chemical, electro chemical and catalytic applications. It is derivatives with large π -electron delocalization have received much attention from materials scientists due to its large second and third order nonlinearities. In the present investigation focused on the synthesis, Growth and characterization of 2-Amino 6-methylpyridinium 6-aminocaproate (2A6M6A) single crystal and its various properties like structural, spectral, optical, thermal and NLO for first time and were studied by using suitable characterization techniques and their results were discussed.

The material selection for industrial applications like in photonics, the key factors not only depend on laser conditions but also on the physical properties of the crystal such as transparency, damage threshold, conversion efficiency, phase matching and temperature stability along with large molecular first hyperpolarizability. Hence a continuous effort is going on in the scientific community to optimize these properties of the crystals for industrial applications.

II. EXPERIMENTAL**A. Material synthesis and Crystal growth**

Analytical pure grade 2-Amino 6-methylpyridine (98%) and 6-Aminocaproic acid (99%) were purchased from SRL and CDH and used for the synthesis of the title material without further purification. The 2A6M6A single crystals with considerable size and good quality are grown in the room temperature using water as a solvent by slow evaporation solution growth method. The precursor's materials of 2-Amino 6-methylpyridine (98%) and 6-Aminocaproic acid (99%)

were taken in the equimolar ratio of 1:1 for the synthesis process is shown in Fig.1. The 6-Aminocaproic acid was first dissolved in the solvent of water, after complete dissolved acid material and then the base compound of 2-Amino 6-methylpyridine was added little by little with the acid solution. The solution is allowed to get a homogenous mixture by continuously stirring for 8 hours using the temperature control magnetic stirrer in the room temperature circumstances. After attaining the homogenous saturated state the solution was filtered using the whatman filter paper which is having the fine holes in the range of 110 μm and the filtered solution was covered with the perforated sheet having the fine holes for the evaporation and it was kept at the room temperature without disturbance. After 2 successive recrystallization process the good quality 2A6M6A crystal was harvested with in the span of 35 days is shown in fig. 2.

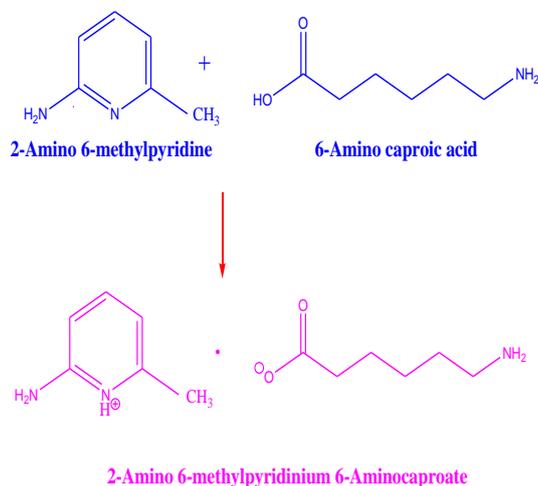


Figure 1. Reaction scheme and chemical structures



Figure 2. A grown crystal of 2A6M6A

B. Characterization techniques

Single crystal X-ray diffraction (XRD) data for 2A6M6A crystal were assessed using Bruker Kappa APEX II diffractometer with $\text{MoK}\alpha$ radiation. PAN analytical X-pert pro diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.540\text{\AA}$) radiation were used to examine powder XRD pattern. The Fourier transform infrared spectrum (FT-IR) of 2A6M6A single crystal was analyzed by Shiraz spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ using a KBr pellet technique. Laser Raman spectrum was taken for the powdered sample in the wavelength range $4000\text{--}400\text{ cm}^{-1}$ using STR 500 mm focal length laser Raman spectrometer. Optical absorption of the grown 2A6M6A crystal was studied using Perkin Elmer Lambda35 spectrometer between 190 and 900 nm. The luminescent spectrum of 2A6M6A crystal was recorded using Shimadzu spectro fluorophotometer (Model: RF-5301 PC) with Xenon arc lamp (150 W) as an excitation source. TG-DTA thermogram was recorded using the PerkinElmer Diamond instrument in a nitrogen atmosphere. 2A6M6A compound is placed in a platinum crucible and the experiment was carried out between the temperature ranges of 30 to 500°C with the heating rate of $10^\circ\text{C min}^{-1}$. The powder SHG efficiency of 2A6M6A was measured using modified Kurtz and Perry method. A Q-switched Nd:YAG laser of wavelength 1064 nm with pulse diameter of 6 mm and pulse rate of 10 Hz with pulse energy of $0.5\text{ }\mu\text{W}$ was used for the measurements.

III. RESULTS AND DISCUSSION

A. Single crystal X-Ray Diffraction study

Single crystal X-ray diffraction analysis is a powerful tool for the determination of the structure of the crystal. Single x-ray diffraction is a non-destructive analytical technique which provides complete detailed information about the internal lattice crystalline materials including cell parameters. The grown crystal 2A6M6A was subjected to the structural characterization by using Bruker Kappa APEX II single crystal diffractometer at 273K with MoK α radiation having the wavelength of $\lambda = 0.71073 \text{ \AA}$. From the single crystal X-ray diffraction analysis, it is observed that the 2A6M6A crystal belongs to the monoclinic crystal system with noncentrosymmetric space group *p*, thus satisfying one of the basic and essential requirement for NLO materials. The cell parameters of the 2A6M6A is found to be $a = 8.54 \text{ \AA}$, $b = 5.89 \text{ \AA}$, $c = 15.24 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 102.86^\circ$, $\gamma = 90^\circ$ and volume $V = 748 \text{ \AA}^3$. The structural parameters of the 2A6M6A crystal were listed in the table 1.

Table 1. Structural parameters of 2A6M6A crystal

Crystal property	2-Amino 6-methylpyridinium 6-aminocaproate
Empirical formula	$C_6H_9N_2^+ \cdot C_6H_{12}NO_2^-$
Crystal system	Monoclinic
Space group	P
Unit cell parameters	$a = 8.54 \text{ \AA}$, $b = 5.89 \text{ \AA}$, $c = 15.24 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 102.86^\circ$, $\gamma = 90^\circ$
Volume of the unit cell	$V = 748 \text{ \AA}^3$
Radiation wavelength	$\lambda = 0.71073 \text{ \AA}$

B. Powder X-Ray Diffraction Analysis

The crystalline nature of the 2A6M6A crystal was characterized by Powder X-ray diffraction analysis to reveal crystalline perfection of the compound. The X-ray diffraction spectrum of 2A6M6A was recorded using the X'pert PRO powder diffractometer with CuK α radiation having the wavelength of $\lambda = 1.5406 \text{ \AA}$. The sample was scanned from the range of 10° to 80° at the rate of $2^\circ/\text{minute}$. The recorded powder x-ray diffraction spectrum is shown in Figure 3. The presence of sharp and well defined peaks confirms the good crystalline nature of 2A6M6A crystal and the corresponding peaks were indexed. The sharp intense peak was found at 23.97° with the crystal faces of (0 0 4).

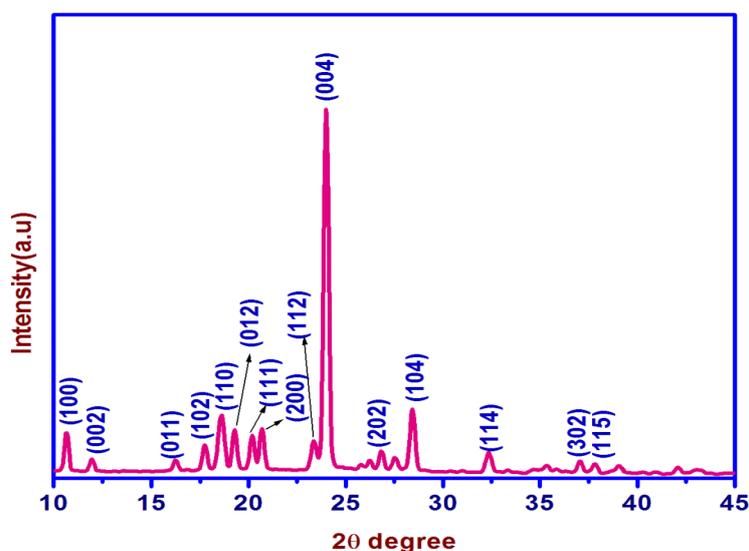


Figure 3. Powder XRD pattern of 2A6M6A crystal

C. FTIR and Laser Raman spectral analyses

The FTIR spectrum was recorded to understand the chemical bonding and it provides useful information regarding the molecular structure of the compound. The KBr pellet technique was used to analyze the sample. FTIR spectrum was taken for the powdered sample in the wavelength range $4000\text{--}400\text{ cm}^{-1}$ using 380 FTIR Spectrophotometer having the resolution of 0.5 cm^{-1} as shown in Fig.4. Laser Raman spectrum was taken for the powdered sample in the wavelength range $4000\text{--}400\text{ cm}^{-1}$ using STR 500 mm focal length laser Raman spectrometer as shown in Fig.5. The observed FTIR and laser Raman bands along with their vibrational assignments are summarized in table 2.

N-H vibrations

According to bellamy [10] vibrational bands in the region of $3000\text{--}3500\text{ cm}^{-1}$ are usually due to the N-H stretching vibrations. In the present investigation small absorption band has observed in the region 3450 cm^{-1} is assigned to N-H asymmetric vibration. This absorption band confirms the nitrogen group present in the compound.

C-H stretching

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region $3000\text{--}3100\text{ cm}^{-1}$ which is the characteristic region for the identification of C-H stretching vibrations [11]. Hence the present investigations the IR peak observed at 3040 cm^{-1} is assigned to the C-H symmetric stretching vibration of the 2A6M6A compound. The peak observed at 2930 and 2860 cm^{-1} in FTIR spectrum, but they were observed at 2895 cm^{-1} in FT-Raman spectrum confirmed the asymmetric stretching of the compound. The C-H out-of-plane and in plane bending vibrations were observed at 839 and 671 cm^{-1} respectively.

C-N stretching

In our present investigation the IR peaks observed at 1050 cm^{-1} and 2220 cm^{-1} and Raman peak at 2107 cm^{-1} represents the C-N stretching vibrations present in the grown 2A6M6A compound.

COO⁻ and C-O stretching

Normally the functional group of COO⁻ stretching vibration is arising between 1550 and 1700 cm^{-1} . In our investigation the peaks observed at 1630 and 1656 cm^{-1} in FTIR and laser Raman due to the asymmetric stretching of COO⁻ group confirms the carboxyl group present in the prepared material [12]. C-O stretching vibration appears as a strong band in the region $1300\text{--}1200\text{ cm}^{-1}$. In this present case the corresponding C-O stretching vibration peaks observed at 1270 cm^{-1} in FTIR and 1057 cm^{-1} in Raman spectrum.

C=C and C-C stretching

The C=C stretching vibrations of the aromatic ring falls at 1470 cm^{-1} in FTIR and 1458 cm^{-1} in Raman spectrum. This medium peak confirms the presence of C=C group present in the title compound [13]. The aromatic C-C stretching vibration occurred in the region $1500\text{--}1400\text{ cm}^{-1}$. In our case the C-C stretching function group is confirmed by 1560 cm^{-1} in FTIR and 1525 in Raman spectrum.

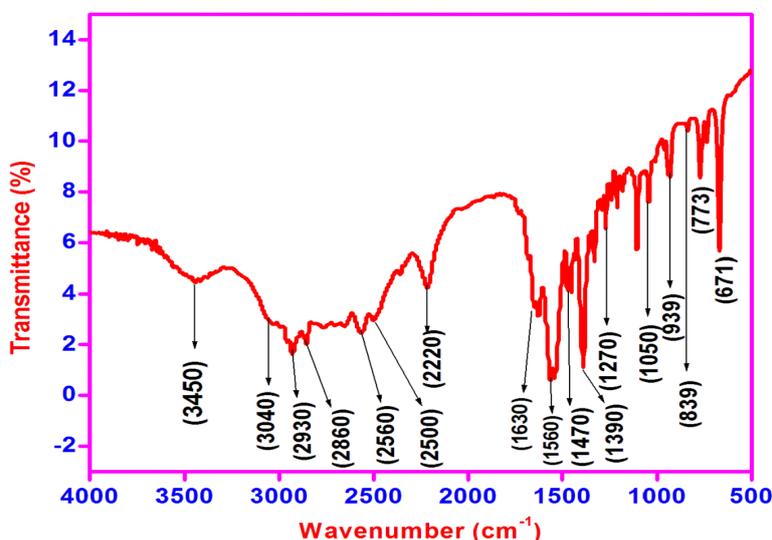


Figure 4. FTIR spectrum of 2A6M6A

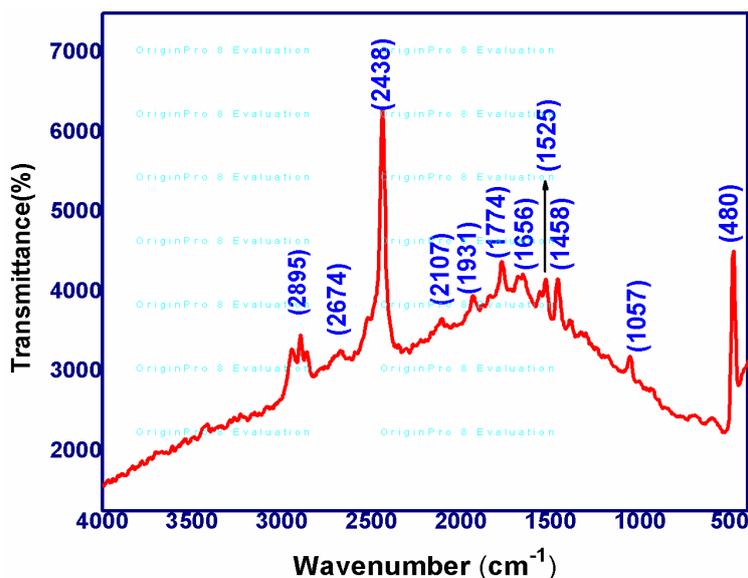


Figure 5. Laser Raman spectrum of 2A6M6A

Table 2. FTIR and Raman frequency assignments of 2A6M6A compound

Wave number (Cm ⁻¹)		Assignments
FTIR	Laser Raman	
3450 cm ⁻¹	----	N-H stretching vibration
3040 cm ⁻¹	----	C-H stretching (Symmetric)
2930 and 2860 cm ⁻¹	2895	C-H stretchin g (Asymmetric)
2220 and 1050 cm ⁻¹	2107	C-N stretching vibration
1630 cm ⁻¹	1656	COO ⁻ stretching vibration
1560 cm ⁻¹	1525	C-C aromatic stretching
1470 cm ⁻¹	1458	C=C stretching vibration
1270 cm ⁻¹	1057	C-O stretching vibration
839 cm ⁻¹	---	C-H out of plane bending
671 cm ⁻¹	---	C-H in plane bending

D. UV- Visible optical Absorption spectral analysis

Studying the optical properties will give extended knowledge about optical transition types, localized states, and electronic band structure of materials [12]. The optical properties such as scattering, light absorption and refractive index are strongly affected by the existence of defects in the grown crystals. So, the crystal with lower scattering center and less absorption defects are needed for practical NLO device fabrications [14]. Since single crystal is mainly used in optical applications, the optical transmissions range and the frequency of cut off wavelength are essential for the optical applications. The optical absorption plays an important role in identifying the potential of the NLO material. The absorption of UV and visible light involves the promotion of electrons in σ and π orbitals from the ground state to higher energy states. The optical absorption spectral analysis of the grown 2A6M6A crystal was carried out using Perkin Elmer Lambda35 spectrometer between 190 and 900 nm. The absorption spectrum of the as grown 2A6M6A crystal is shown in the Figure 6. The UV cut off wavelength of the crystal was found to be at 295 nm. The absence of absorption in the visible region suggests that the crystal possess the good nonlinear optical property.

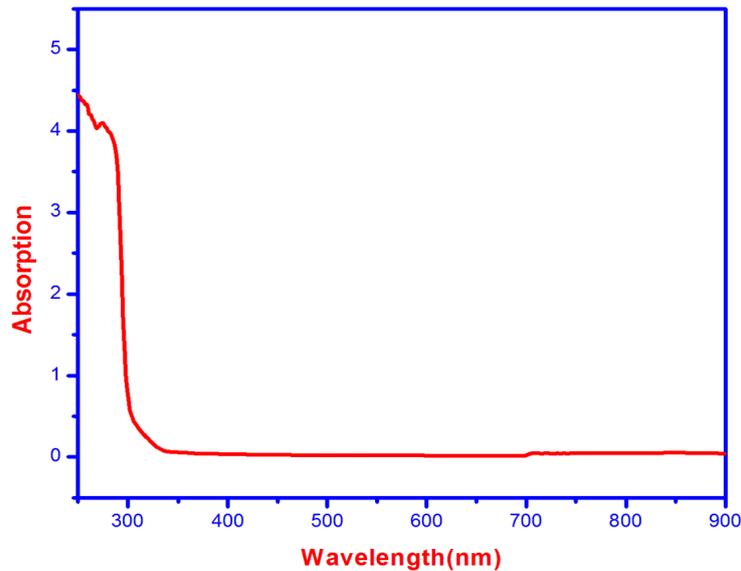


Figure 6. UV-Visible absorption spectrum of 2A6M6A

E. Optical Band gap Energy

For optical device fabrication, the crystal should have high transparency in a considerable range of wavelength [15]. The UV cut-off wavelength of the grown 2A6M6A crystal was found to be 295 nm and it is useful to make them potential material for optical device fabrication. The optical absorption coefficient (α) was calculated using the relation,

$$\alpha = \frac{1}{d} \log \left(\frac{1}{T} \right) \quad (1)$$

Where T is the transmittance and d is the thickness of the crystal. The band gap energy (E_g) was calculated from the following relation [16]

$$(\alpha h\nu)^2 = A (E_g - h\nu) \quad (2)$$

Where E_g is the optical band gap of the crystal and A is a constant. The band gap energy (E_g) was calculated from linear part of the Tauc's plot drawn between $(\alpha h\nu)^2$ and photon energy ($h\nu$). The band gap energy of the grown crystal 2A6M6A was plotted in the Figure 7. The band gap of the 2A6M6A crystal is found to 4.13eV.

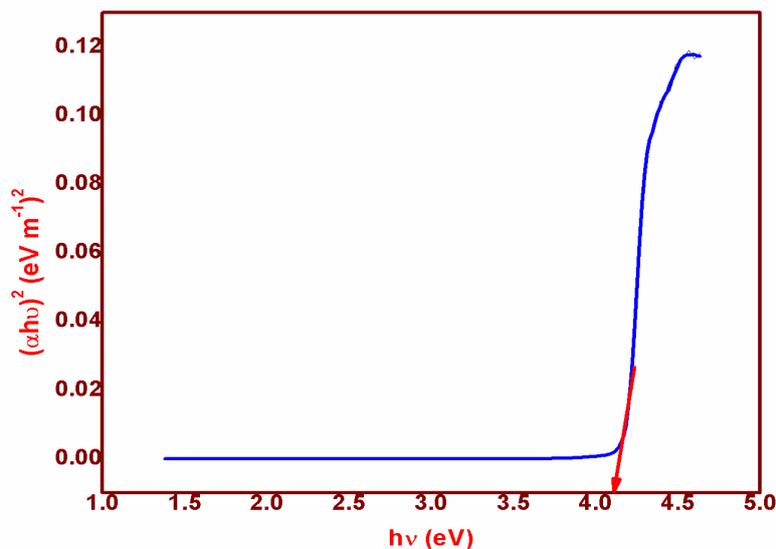


Figure 7. Band gap energy of the 2A6M6A crystal

F. Photoluminescence Studies

Photo luminescence spectroscopy is a non-destructive method for finding out the electronic structure and optical behavior of the prepared materials. It is the mechanism through which an excited specimen relaxes to the equilibrium state. Luminescence process is being excited using a beam of light that leads to the formation of electron
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hole pair and they recombine and emit a photon with the energy equal to the band gap. The PL spectra consist two main parts (i) the near band edge transition region (NBE) usually lying at the ultraviolet transition region (UV) and (ii) the visible light (VL) region related to the deep holes are the reason for the green, yellow and red photo luminescence while the shallow holes are the reason for the violet and blue emissions [17]. The Photoluminescence spectrum of the grown 2A6M6A was recorded in the wavelength region between 380 nm and 520 nm using RF-5301 spectrophotometer is shown in Fig.8. This emission spectrum gives both qualitative and quantitative analyses. The PL spectrum of 2A6M6A grown crystal is excited at 386 nm. From the PL spectrum, two high intensity blue emission peaks and one medium intensity blue emission peak was observed at 460 nm, 487 nm and 420 nm respectively, and it attributes to shallow defects in the band gap and more ordered structure. The sharp high intensity caused because of the similar transition occurring at the various energy levels within the band gap. To achieve a high PL intensity the crystal should be of better quality [18].

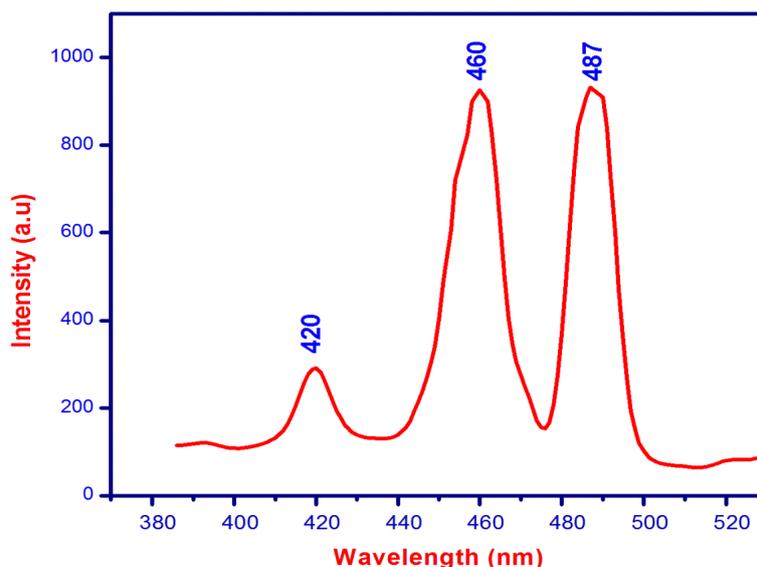


Figure 8. Photoluminescence spectrum of 2A6M6A

G. Thermal Analysis

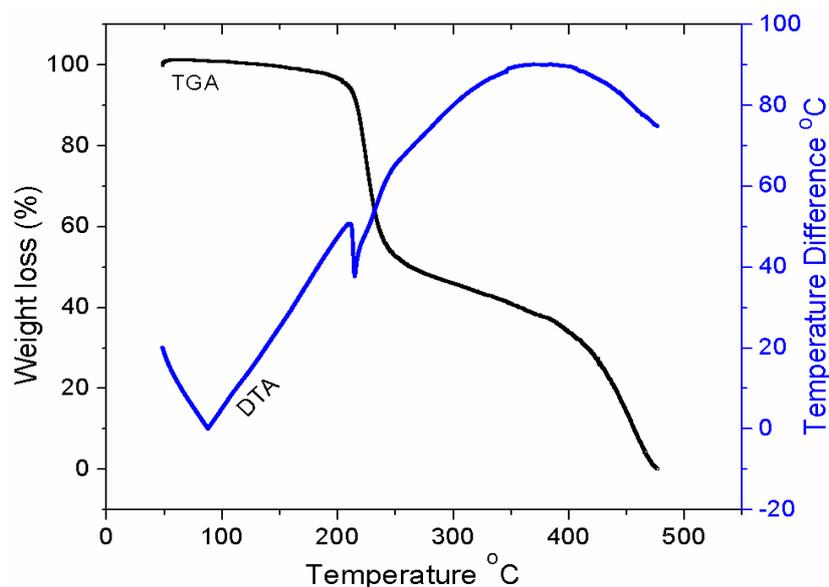


Figure 9. TG-DTA spectrum of 2A6M6A

Analyzing the thermal characterization provide elaborative information on feasible usage of a crystal for NLO device fabrications. To find the thermal characteristics of 2A6M6A, the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were traced with heating rate of 10°C/min in nitrogen atmosphere. The initial sample weight of 1.3 mg was taken and subjected to thermogravimetric analysis between 30 and 500°C. Fig.9. shows the

thermogram of the compound and it illustrates the simultaneously recorded TGA and DTA traces. There is no weight loss observed between room temperature (30°C) and 195°C. This indicates that there is no evaporation on that particular range and found that there is no inclusion of solvent in the crystal lattice. The thermogram reveals that the two stage weight loss, first weight loss starts at 196°C and continues upto 274°C. The second weight loss starts at 385°C and continues upto 479°C. The DTA curve shows a major endothermic peak at 214°C, which corresponds to the complete melting point of the compound. 2A6M6A crystals are ultimately fitted for NLO applications upto 195 °C [19,20].

H. NLO TEST (SECOND HARMONIC GENERATION)

The existence of second harmonic generation in the crystal is affirmed by the green radiation emitted from the material with the intensity of 532 nm wavelength. The molecular structure plays a vital role in determining the degree of SHG response of the material [21]. Kurtz powder SHG test confirmed the nonlinear property of the crystal. A Q switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm and a pulse width of 10 ns repetition rate of 10 Hz was used. The input energy 4.9 mJ/pulse was incident on the crystalline powder. The emission of green light from the 2A6M6A material confirms the phenomena of frequency doubling. The potassium dihydrogen phosphate (KDP) crystal was used as a reference material with the same particle size. The output voltage of the KDP crystal and 2A6M6A material is 8.9 mV and 22.8 mV respectively. Hence from the above discussion Second harmonic efficiency of the 2A6M6A crystal was 2.6 times higher than the potassium dihydrogen phosphate crystal.

IV. CONCLUSION

New organic nonlinear optical single crystal of 2-amino 6-methylpyridinium 6-Aminocaporate (2A6M6A) was synthesized by slow evaporation solution growth method at the room temperature using milliporewater. The single crystal X-ray diffraction studies confirm that the 2A6M6A crystal belongs to monoclinic system with space group P. The crystalline nature was confirmed by powder X-ray diffraction analysis. The chemical construction of the 2A6M6A was confirmed by the identification of the functional group by using FTIR and Laser Raman spectral analyses. The optical absorption spectrum confirms that absence of absorption in the visible region having the cut-off wavelength at 295 nm and band gap energy was found to be 4.13 eV. The Photoluminescence studies revealed that the grown crystal 2A6M6A excited at 386 nm and one medium and two high intensity blue emission peaks appeared at 420 nm 460 nm and 487 nm respectively. Thermal studies shows that the 2A6M6A grown crystal is stable upto 195°C and then the endothermic was observed at 214° C it is closely related to the melting point. The SHG property was analyzed by Kurtz powder method and then the grown crystal is 2.6 times higher than that of KDP crystal and grown crystal is suitable for the optoelectronic applications.

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