Scientific Journal of Impact Factor (SJIF): 5.71

e-ISSN (O): 2348-4470
p-ISSN (P): 2348-6406

International Journal of Advance Engineering and Research Development

International Conference on Momentous Role of Nanomaterials in Renewable Energy Devices

Volume 5, Special Issue 07, April-2018 (UGC Approved)

CRYSTAL GROWTH AND CHARACTERIZATION OF 2-AMINOPYRIDINIUM SALICYLATE ORGANIC NONLINEAR OPTICAL SINGLE CRYSTAL

R. Kaliammal[a], V. Muthulakshmi[b], R. Archana[a], J. Sahaya Melba[a], R. Mohan kumar[c], S. Sudhahar[a,*]

[a]*Department of Physics, Alagappa University, Karaikudi-630003.*
[b]*Department of Industrial Chemistry, Alagappa University, Karaikudi-630003.*
[b]*Department of Physics, Presidency College, Chennai-600005*.

ABSTRACT - *Organic nonlinear optical (NLO) crystals of 2aminopyridinium salicylate have been grown by slow evaporation growth technique using acetone: water mixed as solvent. The crystal structure, lattice parameters and crystalline perfection were confirmed by Single crystal and powder X-ray diffraction analyses. The functional groups and chemical composition of grown 2ASA crystal was confirmed by FTIR analysis. UV-Vis spectral study showed that grown crystal has high transparency (~82%) in the entire visible region and the cut off wavelength at 360 nm. PL spectral study of grown 2ASA showed an intense emission peak at 362 nm for an excitation wavelength at 340nm. The SHG relative efficiency of 2ASA crystal has been found 1.19 times higher than that of KDP. Thermal analysis reveals that 2ASA is thermally stable up to 150°C.*

Keywords: *Crystal structure, Orgonic crystal, Optical studies, Nonlinear optical, Thermal analysis.*

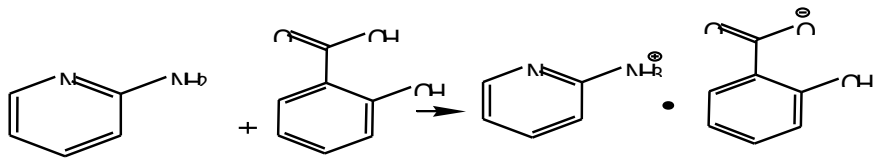
I. INTRODUCTION

In the recent years many kinds of organic nonlinear optical materials with variety of design possibilities, large NLO efficiencies, high electro-optic coefficient, low dielectric constant have attracted great interest because of their applications in electro optic modulators, optical information processing, optical memory and the generation of THz radiation [1-3]. Compared to inorganic materials, organic materials posses high laser damage threshold, large hyperpolarizability and fast response to electro optic devices. In particular, π-conjucated systems linking a donor (D) and acceptor (A) show a large NLO response and have been intensively investigated [4-8]. In particular the strong delocalization of electronic charge distribution and H- bonding leads to a high mobility of the electron density causes the large molecular hyperpolarizability and the nonlinear susceptibility in the organic molecules [9]. Organic ionic crystals with hetero aromatic electron acceptor such as pyridinium, imidazolium and quinolinium posses a strong electron withdrawing characteristics exhibits large second and third order nonlinear responses [10]. Due to excellent physicochemical properties of amino acid family crystals they are subjected to extensive investigation by many research scientists. Particularly in the view of NLO application organic amino acids are interesting because they contain donor carboxylic (COOH) group and the proton acceptor (NH_2) group known as zwitterions which creates hydrogen bonds. This kind of dipolar nature of amino acids proved as an ideal candidate for NLO applications [11-13]. 2-aminopyridine is an organic heterocyclic molecule which is often used as a ligand in a metal complex and also as a model compound for understanding nucleic acid bases [14-15]. In the present investigation 2-aminopyridinium salicylate organic nonlinear optical single crystal were grown by the slow evaporation technique and its various properties like structural, spectral, optical, thermal and NLO were studied by using suitable characterization techniques and their results were discussed.

II. EXPERIMENTAL SECTION

A. MATERIAL SYNTHESIS AND CRYSTAL GROWTH

The title compound of 2-aminopyridine (C5H6N2) and salicylic acid (C7H6O3) regents were used for the synthesis of 2-aminopyridinium salicylate (2ASA) compound. 2ASA crystals were grown by the slow evaporation solution growth technique at room temperature. Salicylic acid was first dissolved in acetone throughly by continuous stirring and then the measured amount of 2-aminopyridine was added and dissolved in distilled water. The solution was stirred for about 12 hour to complete the reaction process. The homogeneous solution was filtered using filter paper and then it was allowed for slow evaporation solution growth technique. The tiny crystal was formed at the bottom of the container due to spontaneous nucleation within 30-35 days. Good optical quality crystals were harvested after a period of 35-50 days. The synthesized compound was recrystallization at least two times in acetone to improve the purity of the compound. The photograph of as grown crystal of 2ASA is shown in fig.2.



2aminopyridine salicylic acid 2aminopyridinium salicylate

Figure 1. Reaction scheme and chemical structure

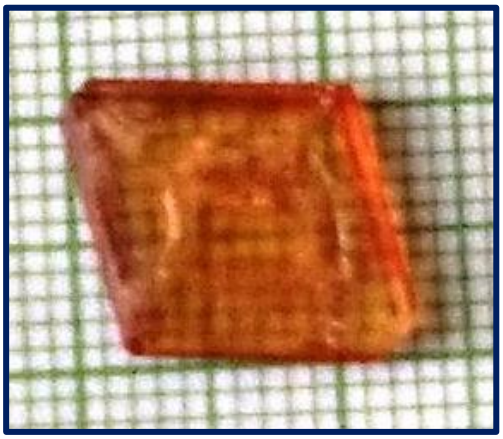


Figure 2. Photograph of as grown 2ASA crystal

III. RESULT AND DISCUSSION

A. Structural Analyses

Table.1. Structural parameters of 2ASA crystal

Crystal data	2ASA
Empirical formula	$(C_5H_7N_2)^+.(C_7H_5O_3)^-$
Formula weight	138.122g/mol
Crystal system	Tetragonal
Space group	P
Unit cell dimension	a=11.88Å, b=11.87 Å c=16.02Å α=90.24°, °, γ =90.20° β=90.07°
Volume	V=2260Å^3
Temperature(K)	295
Radiation[Å]	MoKα (0.71073)

Single crystal X-ray diffraction is a non-destructive analytical technique which provides the detailed information about the internal lattice of crystalline materials, including cell dimensions, bond –lengths, bond angles and site-ordering. Directly related single-crystal refinement, where the data generated from the X-ray analysis is interpreted to obtain the

crystal structure. X-ray powder diffraction is a powerful tool for the study of crystalline materials. Each crystalline material shows a district X-ray diffraction pattern due to the difference in the lattice parameters, atom types and packing of molecules. Bruker kappa APEXII single crystal X-ray diffractometer with MoKα radiation was used to measure the cell parameters of 2ASA crystal. X-ray powder diffraction pattern of 2ASA crystal was recorded using Expert Pro with CuKα radiation. X-ray diffraction study was carried out at 293k. ASA crystal belongs to tetragonal crystal system with centrosymmetric. The estimated lattice parameters are a=11.84Å, b=11.87Å, c=16.02Å, α=90.24°, β=90.07°, γ=90.20° and volume V=2260Å^3. The 2ASA crystal was crushed into a uniform fine powder and was subjected to powder X-ray diffraction study to reveal the crystalline perfection of compound. The sharp and intense peaks revealed the high crystalline of the grown crystal and the corresponding peaks were indexed. The recorded powder X-ray diffraction pattern of 2ASA crystal is shown in fig.3.

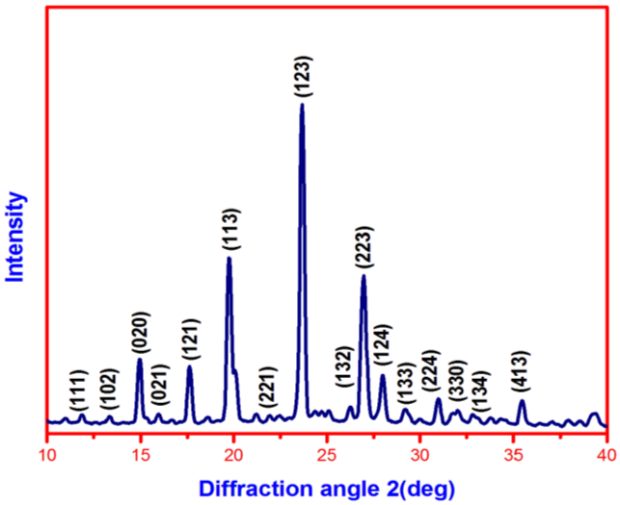


Figure 3. XRD pattern of the 2ASA crystal

B. FTIR SPECTAL ANALYSIS

The FTIR spectrum was recorded to band position, shape and it provides useful information regarding the molecular structure of compound. In phenols the free O-H group absorbed at 2718 cm^{-1}. While the associated group has a stretching frequency in the range (2500-3000) cm^{-1}, this is due to the intermolecular hydrogen atom. The hetero atomic compounds showed that the presence of C-H stretching vibration in the region (3000-3100 cm^{-1}) for the ready identification C-H stretching vibration. The stretching mode of 2ASA was observed at 3081cm^{-1} in FTIR spectrum. The molecule under consideration is a secondary amine and hence N-H stretching vibrations are possible. Hetero aromatics containing N-H stretching vibration peak observed at 3289 cm^{-1}. The rings C-O and C-C stretching vibration are very much important in the spectrum. The ring carbon-oxygen stretching vibrations occurred in the region 1672cm^{-1}. The ring carbon-carbon stretching vibrations occurred in the region (1150-1250) cm^{-1} in the ASA compound was observed at 1140 cm^{-1} is due to the aromatic carbon-carbon stretching mode in FTIR spectrum The C-H bending bands occur between 860-680 cm^{-1}.This peak absorbed at 859 cm^{-1} shows the strong absorption of aromatic C-H bending vibrations.

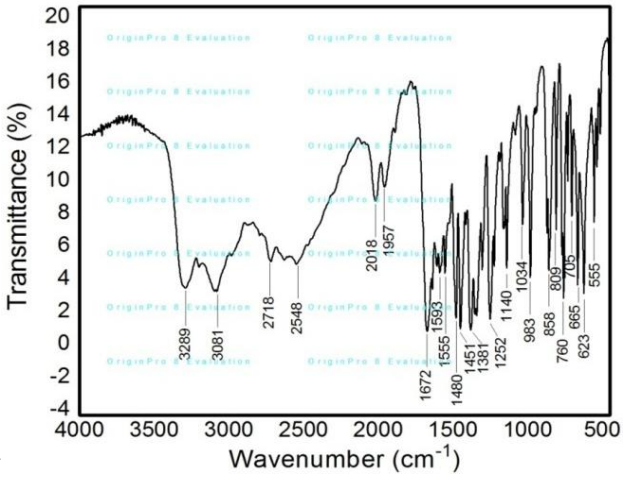


Figure 4. FTIR spectrum of 2ASA crystal

Table 2. FTIR vibrational assignments of 2ASA crystal

Wavenumber (cm^{-1})	***Assignments***
3289	N-H stretching secondary amine
3081	C-H stretching
2718	Strong O-H stretching carboxylic acid
1555	C=C stretching
1488	C=C asymmetric stretching vibration
1272	C-O stretching vibration
1140	C-C stretching
859	C-H bending

C. UV-Vis transmission spectral analyses

Optical transmission and cut-off wavelength of a crystal are important physical parameters for optical applications. The optical behaviour of ASA crystal specimen was analysed using UV-Vis spectrophotometer in the wavelength range of 190-900 nm is shown in fig.5. The extended transmission window will enable higher harmonic generations and wavelength extension by cascaded frequency conversion process. For linear and nonlinear optical applications, the material must be transparent in the wavelength region of specific interest. The thickness of 0.3 mm crystal was used for this study. The 2ASA crystal transmittance in the visible and IR regions and has good transparency of about 82%. From the spectrum the cut off wavelength for the grown crystal was found to be 360 nm. UV-Visible study suggests that 2ASA material is a good candidate for second harmonic generation and optoelectronic applications.

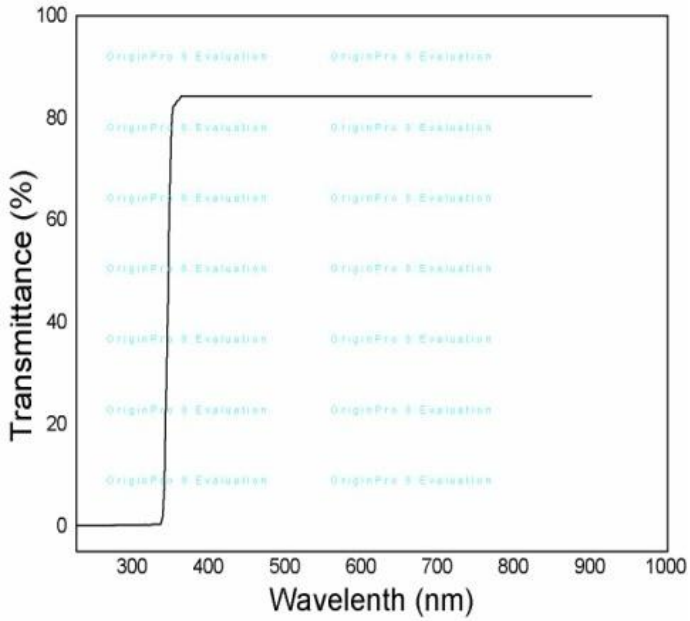


Figure 5. UV-Vis transmission spectrum of ASA crystal

D. Optical bandgap studies

The optical absorption coefficient with the photon energy helps to study the band structure and types of transition of the electrons. From the transmission data, the optical absorption coefficient (α) was calculated using the relation,

$$\alpha = (1/d) \log (1/T)$$

Where d is the thickness of the crystal and T is the transmittance. As a direct bandgap material, an absorption coefficient (α) obeying the following relation for high photon energies (hν),

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

where E_g is the optical bandgap of the crystal and A is a constant. The bandgap energy were calculated from linear part of the Tauc's plot drawn between $(\alpha h\nu)^2$ and photon energy (hν).The linear portion of the plot at the absorption edge

confirms that the crystal has a direct optical band gap. The bandgap energy of the grown crystal 2ASA was plotted in the fig.6. The bandgap of the 2ASA crystal is found to be 3.6eV.

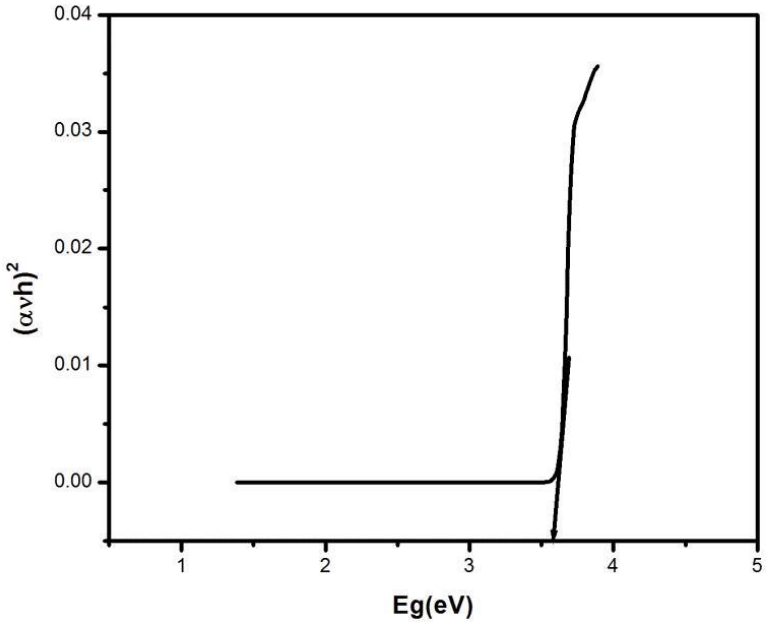


Fig.6. Bandgap energy of 2ASA crystal

E. Photoluminescence studies

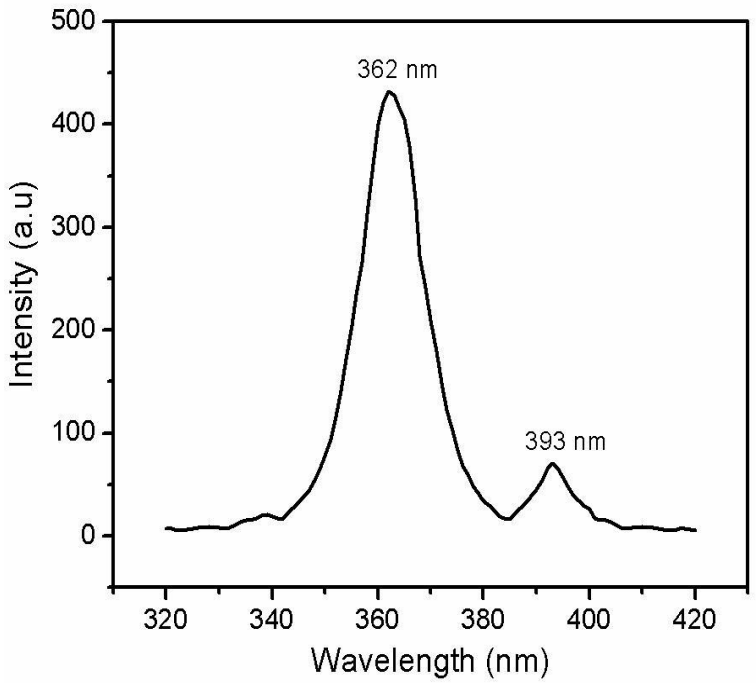


Figure 7. PL spectra of 2ASA crystal

Photoluminescence spectroscopy is one of the effective tools to provide relatively direct information about the physical properties of the material at the molecular level, including shallow and deep level defects and gap states. Photoluminescence is a process in which a chemical compound absorbs a photon with a wavelength in the range of visible electromagnetic radiation , thus transitioning to higher electronic energy state, and then radiates a photon back out, returning to a lower energy state. Photoluminescence excitation spectrum of 2ASA was recorded in the wavelength range between 320 and 420 nm with an excitation wavelength of 340 nm, it was observed from the PL spectra that ASA compound exhibits a stronger UV band peak in the emission. The emission spectrum provides information on both qualitative and quantative analyses. A very strong intense blue emission peak was observed at 362 nm, which corresponds to near band-edge excitons of grown crystal.

The energy bandgap was estimated at this wavelength of 362 nm as 3.6eV using the formula

$E_g = hc/\lambda p$

h, c, p------- constant

λ---------- wavelength of flourescence [16].

3.6 Thermal analyses

Thermogravimetric and differential thermal analyses (TG-DTA) measurements were used to examine the thermal stability of the crystalline sample and to define the conditions for the thermal treatment. TG-DTA thermograms were traced for 2ASA compound in nitrogen atmosphere with heating rate of 20°C/min. The 2ASA sample weighed 2.962 mg was used to observed that there is no weight loss before 150°C. TG curve shows that a single stage weight loss pattern is seen from 151°C to 250°C in this region all the groups are decomposed. Thus the TGA curve indicates that the sample is stable up to 150°C. In the DTA curve, one prominent endothermic peak was observed at 200°C. Hence, the recorded thermograms confirmed that the title compound is thermally stable up to 150°C.

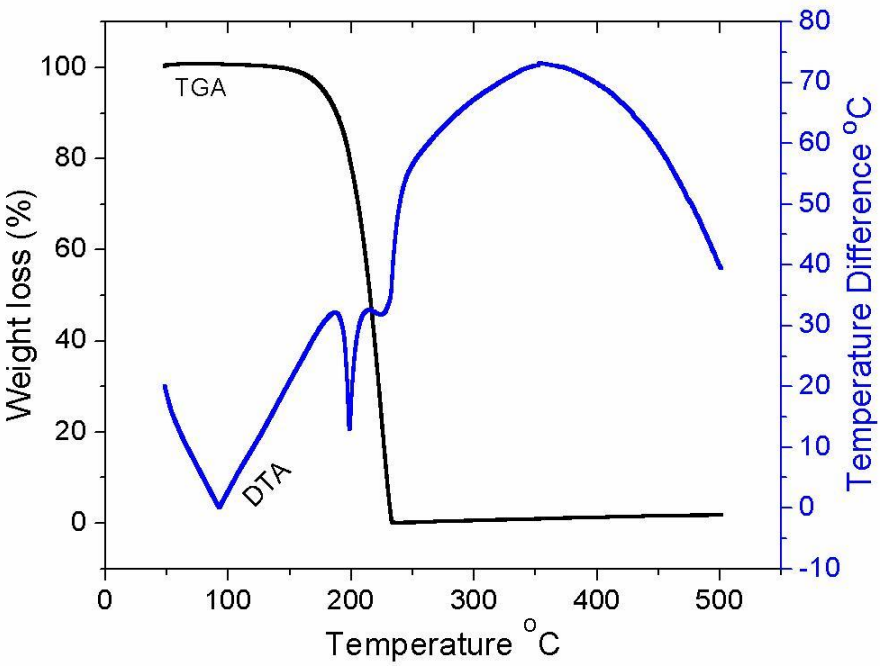


Figure 8. TG-DTA spectrum of 2ASA crystal

F. Second Harmonic Generation Studies

The second harmonic generation efficiency of 2ASA crystal was measured by using Kurtz-perry powder SHG technique with KDP crystal as reference material [17]. The fundamental Q-switched Nd:YAG laser was used as a light source. A laser beam of fundamental wavelength 1064 nm with10ns pulse width, 10Hz pulse rate was focused on the sample. The input energy incident on the powdered sample was chosen to be 4.9mJ/pulse. The output voltage of the KDP crystal and ASA compound was observed generation value of 8.9mV and 10.6mV respectively. SHG efficiency of the 2-aminopyridiniumsalicylate was 1.19 times higher than KDP crystal.

IV. CONCLUSION

The new organic crystal 2ASA was grown in low temperature solution growth by slow evaporation method. From the single crystal analysis, it was observed that the grown crystal belongs to tetragonal crystal system with noncentrosymmetric space group P. The estimated lattice parameters a=11.88Å, b=11.87Å, c=16.0Å, α=90.24°, β=90.07°, γ=90.20° and volume V=2260Å^3. The presence of functional groups of the grown 2ASA crystal was analyzed using FTIR spectral studies. UV-Vis transmittance studies revealed the transparency, cut off wavelength and band gap energy of the grown crystal. The extended transmission window will enable higher harmonic generations and wavelength extension by cascaded frequency conversion process. From the spectrum the cut off wavelength for the grown crystal was found to be 360 nm. The bandgap was determined and the bandgap value is 3.6 eV. The photoluminescence behaviour of 2ASA crystal was observed and for the excitation wavelength is 340 nm. The relative SHG efficiency of 2ASA crystal was found to be 1.19 times that of standard KDP crystal. The recorded thermograms confirmed that the title compound is thermally stable up to 150°C.

REFERENCES

[1]. Y. Shi, C. Zhang, H. Zhang, J.H. Bechtel, L.R. Dalton, B. Robinson, W. Steier, Low (sub-1-volt) halfwave voltage polymeric electro-optic modulators achieved by controlling chromophore shape, *Science.* 288(2000) 119-122.
[2]. A.F. Benner, M.Ignatowski, J.A. Kash, D.M. Kuchta, M.B. Ritter, Exploitation of optical interconnects in future server architectures, IBM. *J. Res. Dev*. 49 (2005) 755-775.
[3]. A. Schneider, M. Neis, M. Stillhart, B. Ruiz, R. khan, P. Gunter, Generation of terahertz pulses through optical rectification in organic DAST crystals : theory and experiment, *J. Opt. Soc. Am. B*. 23(2006) 1822-1835.
[4]. G. Shanmugam, S. Brahadeeswaran, Spectroscopic, thermal and mechanical studies on 4-methylanilinium p-toluenesulfonate – a new organic NLO single crystal, S*pectrochim. Acta A: Mol. Biomol. Spectrosc*, 95 (2012) 177-183.
[5]. L.Guruprasad, V. Krishnakumar, R. Nagalakshmi, S. Manohar, physicochemical properties of highly efficient organic NLO crystal: 4-Aminobenzamide, *Mater. Chem. Phys*. 128 (2011) 90-95.
[6]. P. Krishna, K. Gayathri, N. Sivakumar, S. Gunasekaran, G. Anbalagan, Nucleation kinetics, growth, crystalline perfection, mechanical, thermal, optical and electrical characterization of brucinium 2-carboxy-6-nitrophthalate dihydrate single crystal, *J. Cryst. Growth*, 396(2014) 85-94.
[7]. Amirdha sher Gill, S.Kalainathan, Thermal, optical, mechanical and dielectric properties of nonlinear optical crystal 4-methoxy benzaldehyde-N-methyl 4-stilbazolium tosylate, *J. Phys. Chem. Solids*, 72 (2011) 1002-1007.
[8]. D.Joseph Daniel, P. Ramasamy, Studies on the nonlinear optical single crystal: Ammonium D,L-tartrate(C4H9NO6) *Mater. Res. Bull.* 47 (2012) 708-713.
[9]. V. Crasta, V. Ravindrachary, R.F. Bhajantri, R. Gonsalves, *J. Cryst. Growth*, 267 (2004) 129-133.
[10]. Seung Heon Lee, Ba-Wool Yoo, Hoseop yun , Mojca Jazbinsek, O. Pil Kwon, *J. MoL Struc*. 1100 (2015) 359-365.
[11]. Srineevasan R and Rajasekaran R., *Journal of optoelectronics and Advanced Materials*, 16 (2014) 65-69.
[12]. Ushashree P.M., Muralidharan R., Jayavel R., Ramasamy P., *J. Crystal Growth*, 210 (2000) 741-745.
[13]. Maadeswaran P., Thirumalairajan S., Chandrasekaran, *Optik*, 121 (2010) 1620-1624.
[14]. P.V. Dhanaraj, N.P. Rajesh, G. Vinitha, G. Bhagavannarayana, Crystal structure and characterization of a novel organic optical crystal : 2-Aminopyridinium tricholoroacetate, *Mater. Res. Bull*. 46 (2011) 726-731.
[15]. P.V. Dhanaraj, N.P. Rajesh, G. Bhaghavannarayana, Synthesis, crystal growth and characterization of an organic NLO material: Bis(2-aminopyridinium) maleate, *Physica B*, 405 (2010) 3441-3445.
[16]. B. Deepa, P. Philominathan, Optical, mechanical and thermal behaviour of Gudinium carbonate single crystal, *optik*, 127 (2016) 1507-1510.
[17]. P.Prabukandhan , R. Lakshmi , G.Harichandran , C.Sudarshana Kumar, Synthesis, structural, optical and thermal properties of N-methyl-N-aryl benzamide organic single crystals grown by a slow evaporation technique, *J. MoL. Struc*., 1156 (2018) 62-73.