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# Growth, Structural, Optical, Thermal And Mechanical Studies Of Semicarbozidehydrochloride Adipate For Nonlinear Optical Applications

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***Abstract***

Non- linear optical crystals have a great impact on information technology and industrial applications.The present paper deals with the growth and characterization of Semicarbozidehydrochloride adipate (SCHA). An organic non-linear optical material of SCHA was synthesized ethanol as a solvent .The single crystals were grown by slow evaporation technique at room temperature. The cell dimensions obtained by single crystal X-ray diffraction studies reveal that the crystal belongs to the orthorhombic system. The occurrence of prospective functional groups was initially identified by FTIR and FT-Raman spectroscopic studies. The optical transparency of the crystals was determined by UV- Visible studies in the wavelength range of 200-1200 nm. Second harmonic generation conversion efficiency found using the Kurtz and Perry method is about 4.2 times that of KDP. The thermal stability of the compound was determined by TG-DTA analysis of the specimen. The microhardness test was carried out and the load dependent hardness was measured.

*Key words*: X-ray diffraction, FT-IR, Optical transmission, Second harmonic generation,

TGA/DTA

## I. INTRODUCTION

In the modern world, the development of functional materials with desirable properties is intensely facilitating the fast-growing multi-disciplinary research areas like nonlinear optics (NLO), dielectric, piezoelectric, pyroelectric and ferroelectric [1]. Over the last few decades, the nonlinear optical (NLO) single crystals play an inevitable role in a wide range of technological applications such as lasers, optoelectronics, information processing, optical data storage, optical switching, THz generation and detection [2 - 4]. The rapid advancements in photonic and optoelectronic devices strongly depend on the ease of design and fabrication of the NLO single crystals. In recent scenario the fast developing fields photonics and optoelectronics are mainly focusing on nonlinear optical (NLO) materials because they are widely used for second harmonic generation, optical bi-stability, laser remote sensing, optical disk data storage, laser driven fusion, medical and spectroscopic laser, photonic integrated circuitry, optical

parametric oscillations. Also, the grown crystals should possess a large size with high quality and low economical aspects. In this regard, the large demand for growing NLO single crystals is increasing day by day. Therefore, the crystal growth researchers are still putting enormous efforts into the design and development of novel organic, inorganic and semi-organic single crystals to attain high performances in real-time NLO devices.

Today, crystal growth technology has advanced rapidly for the development of novel nonlinear optical materials for various applications such as optical switching, frequency conversion and elect optical modulation [5 - 7]. Organic crystals are of great interest for the nonlinear optical technologies in line with the tendency to replace the classical electronics with organic materials. The design and synthesis of new organic crystals with NLO properties both in solution and in bulk is the first step. The novel organic compound with NLO properties and better efficiency, transparency trade off is of current interest [8].

## II. EXPERIMENTAL

### 2.1. Material synthesis and crystal growth

The Semicarbozidehydrochloride and adipic acid was dissolved in 100 mL of ethanol solvent contained in a 250 mL beaker and stirred well using a magnetic stirrer to get a homogeneous solution [9,10]. The saturated solution was filtered using Whatman filter paper to remove suspended impurities and tightly covered by polythene paper. Some holes were made in the polythene paper to achieve slow evaporation. The synthesized compound was purified by recrystallization process three times to minimize the impurity of the materials since high-quality crystals are necessary to evaluate the NLO properties of materials. In this work, slow evaporation technique was used to grow Semicarbozidehydrochloride adipate (SCHA) single crystals. Scheme of the chemical reaction of SCHA is shown in Fig. 1. Good transparent colorless single crystal was harvested in a growth period of 20 days with the dimensions of 12 × 10 × 2 mm. Photograph of as grown SCHA crystal is shown in Fig. 2.

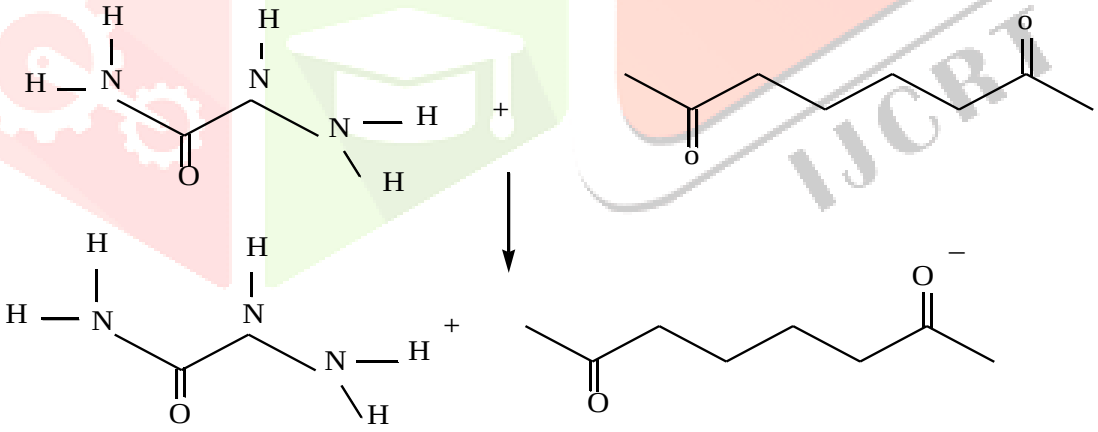

Fig. 1. Scheme of the chemical reaction of SCHA

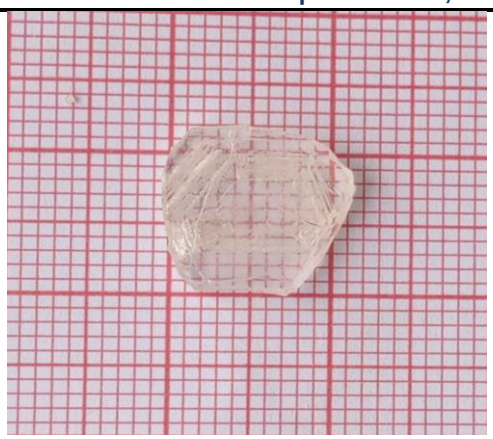

Fig. 2. Photograph of SCHA crystal

2.2. Characterization

The grown SCHA single crystal was subjected to various characterization techniques like single crystal X-ray diffraction, Fourier transform infrared (FTIR), FT – Raman, UV – VIS – NIR, Fluorescence studies, Microhardness studies, thermal analysis, melting point measurement and nonlinear optical studies [11 – 13]. Single crystal X-ray diffraction studies have been carried out using Enraf Nonius CAD4 diffractometer with MoKα (λ=0.7170 Å) to determine the cell parameters. The optical transmission spectrum of SCHA single crystals has been recorded in the region 200–1100 nm using a Shimadzu UV-1061 UV–vis spectrometer. The coordination of Semicarbozidehydrochloride and adipic acid was confirmed by FTIR studies using BRUKER 66 V FT-IR spectrometer in the range 4000 – 400 $cm^{-1}$ following KBr pellet technique. The thermal characterization was determined by thermogravimetric analysis and differential thermal analysis using a SDT Q600 V8.0 thermal analyzer in a nitrogen atmosphere. The melting point of the material was confirmed by melting point apparatus. The NLO property of the crystal was confirmed by Kurtz powder second harmonic generation (SHG) test. FT – Raman spectrum of the SCHA was recorded on a BRUKER RFS 27 FT – Raman spectrometer equipped with an FRA-106 FT – Raman accessory in the region 4000 – 0 $cm^{-1}$. The strength of the materials for device fabrication is explicitly dependent on an important parameter called hardness [14 – 18]. The mechanical hardness was estimated by Vicker's micro hardness tester. The excitation and emission spectrum for SCHA was recorded using Varian Carry Eclipse Fluorescence spectrometer.

III. RESULT AND DISCUSSION

3.1. Single crystal X-ray diffraction

One of the good quality harvested crystals was selected for single crystal X-ray diffraction analysis to determine the lattice parameters using BRUKER KAPPA APEX II CCD difractometer with MoKα (λ = 0.71073 Å). X-ray diffraction studies confirmed that the SCHA crystallizes in orthorhombic system with noncentrosymmetric space group P1. The measured unit cell parameter values are a = 4.67Å, b = 7.58Å, c = 13.19 Å, α = β = γ = 90° and volume = 467$Å^3$.

3.2. FTIR spectral analysis

Perkin Elmer spectrometer was used to record FT-IR spectrum of SCHA crystal in the range 400 - 4000$cm^{-1}$ which was in the form of solid dispersed KBr pellet method [19 - 22]. The recorded spectrum was used to identity various functional groups depicted in Fig. 2. The molecular interactions between the reagents can be well explained by examining different modes of vibrations and deformations like stretching, wagging, bending. In the higher energy region the peak at 3723 $cm^{-1}$ is assigned to NH asymmetric stretching. The CH asymmetric stretching vibration appears at 3093 $cm^{-1}$. The $CH_2$ asymmetric stretching vibration occurs at 2837$cm^{-1}$. The C=O stretching appears at1685 $cm^{-1}$. The $CH_2$

bending mode is due to 1424 $cm^{-1}$. The aromatic ring skeletal vibration occurs at 1591 $cm^{-1}$. The $CH_3$ bending modes appears at 1309 $cm^{-1}$. The $CH_2$ wagging vibration produces a sharp intense peak at 1239 $cm^{-1}$. The peak at 1128 $cm^{-1}$ assigned to C – C stretching vibration. The C –N stretching vibration produces its characteristics peak at 1089 $cm^{-1}$. The C – H symmetric stretching vibration appears at 928 $cm^{-1}$. The out of plane aromatic C – H bond occurs at 761 $cm^{-1}$.

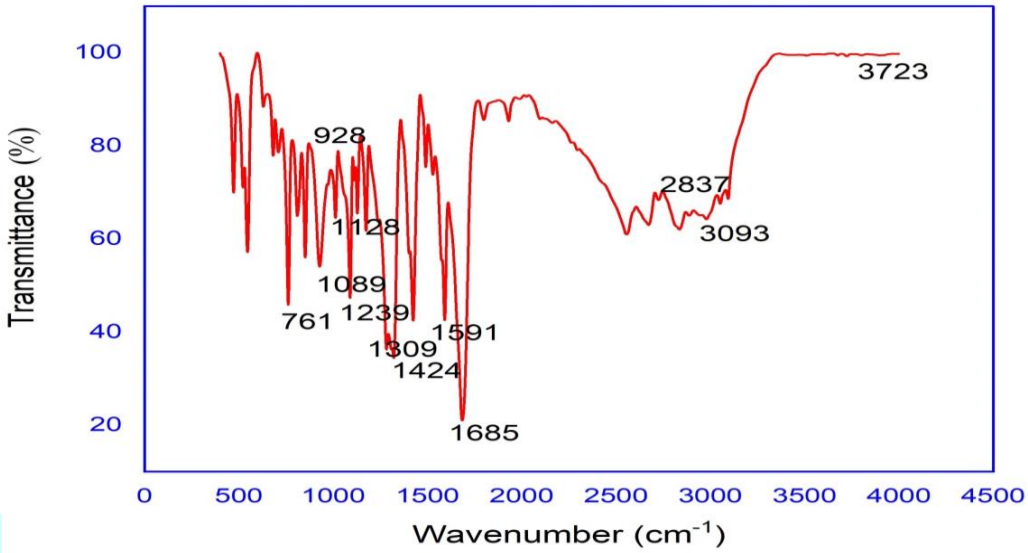


Fig. 2. FTIR spectrum of SCHA crystal

3.3. FT Raman spectral analysis

The Raman spectrum of the compound given in Fig. 3. The CH asymmetric stretching vibration appears at 3094 $cm^{-1}$. The N–H stretching occurs at 2919 $cm^{-1}$. The aromatic ring C– H stretch is observed at 1646 $cm^{-1}$ as an intense sharp peak. The C=O stretch also shows a sharp peak at 1410 $cm^{-1}$. The peak at 1300 $cm^{-1}$ is due to aromatic ring skeletal vibration. The $CH_2$ asymmetric stretch observed as a sharp signal at 1248 $cm^{-1}$ and the C-H symmetric stretch is observed as an intense peak around 1049 $cm^{-1}$. The C-N stretch is assigned to the peak at 914 $cm^{-1}$. The peak at 508 $cm^{-1}$ in the lower number regions is due to C-H bending mode [23 – 25].

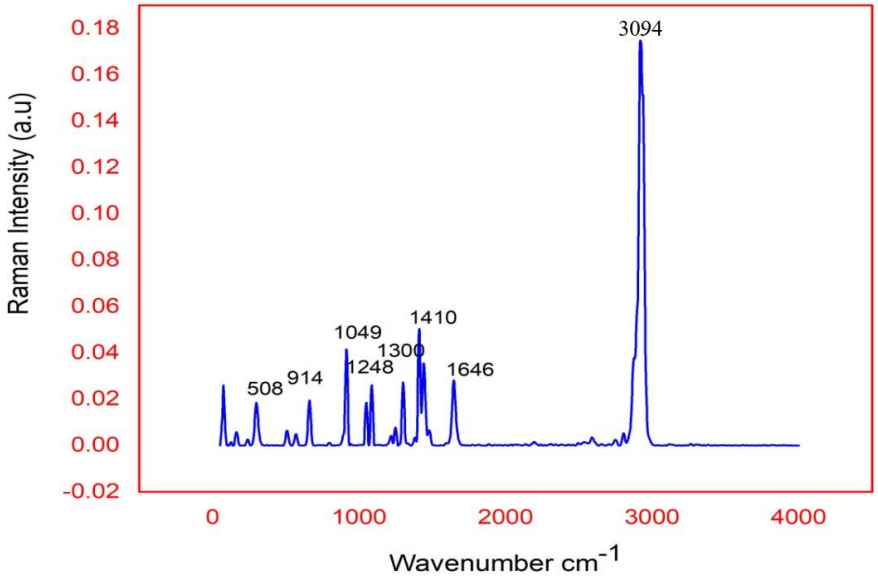


Fig. 3. FT – Raman spectrum of SCHA

3.4. UV–VIS–NIR study

Optically polished crystal of 2 mm thickness was used for the study. The obtained transmission spectrum is shown in Fig. 4. The sample possesses a wide transparency from 200 to 1200 nm is approximately 92% and the upper cut off wavelength is found at 236 nm. The absence of absorption in the visible region confirms to the colourless nature of the crystal and it is the key requirement for materials having NLO properties [26 - 28].

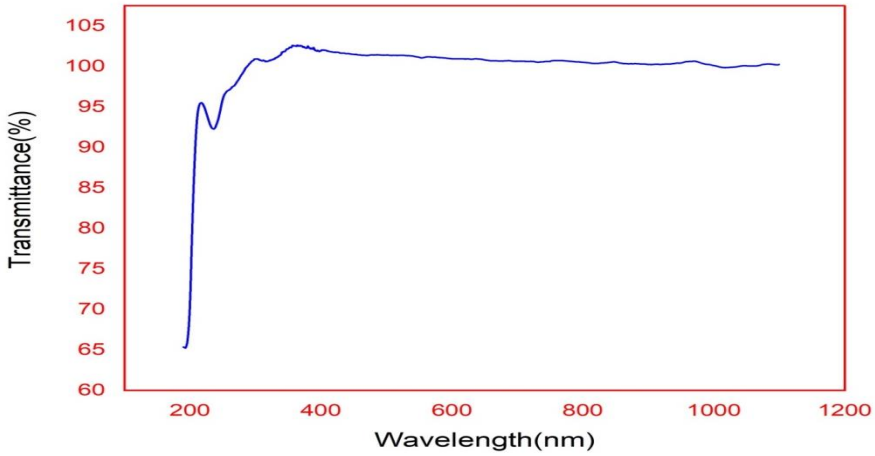


Fig. 4. UV-visible spectrum of SCHA

3.5. Fluorescence study

Fluorescence may be expected generally in molecules that are aromatic or contain multiple conjugated double bonds with a high degree of resonance stability. Fluorescence finds wide application in the branches of biomedical, medical and chemical research fields for analysing organic compound. The excitation spectrum was recorded in the range 200 -1000 nm and it is shown in Fig. 5. The first sharp peak appears at a wavelength of 364 nm and it emits ultraviolet colour. The second sharp peak appears at 532 nm it emits green colour and the third small peak at 713 nm it emits red colour [29, 30]. A higher power ratio in the luminescence spectrum is an evidence of better purity, crystalline and structural perfection of the SCHA crystal. Hence this organic molecule with promising fluorescence emission can be exploited for NLO applications.

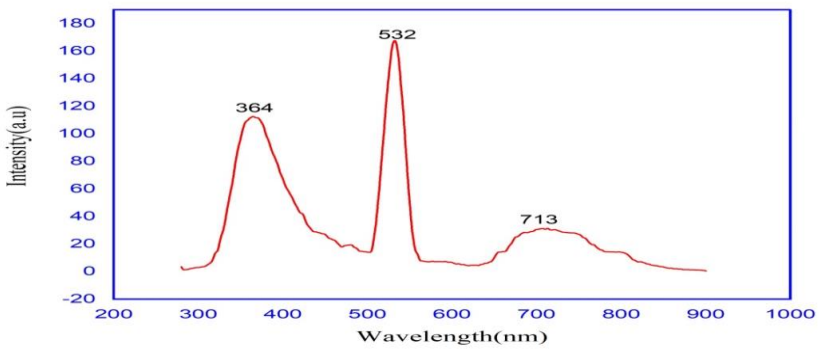


Fig. 5. Fluorescence spectrum of SCHA

3.6. Microhardness study

In order to understand the plasticity of the crystals, micro hardness tests were carried out on the grown crystals. The hardness of the crystals depends on type of chemical bonding, lattice energy, Debye temperature, heat of formation and interatomic spacing [31]. The good quality crystals are needed not only with good optical performance but with good mechanical behaviour. Hardness of the material is the resistance it offers to indentation by a much harder body. Microhardness measurements were done for SCHA crystal using Leitz-Wetzlar hardness tester fitted with a vicker's diamond indenter at room temperature. When the mean diagonal of the indentation has been determined, the hardness was calculated using the relation [32].

$$H_V = 1.8544\ P/d^2$$

Where $H_V$ = Vicker's hardness number, P = load in g, d = diagonal length in mm.

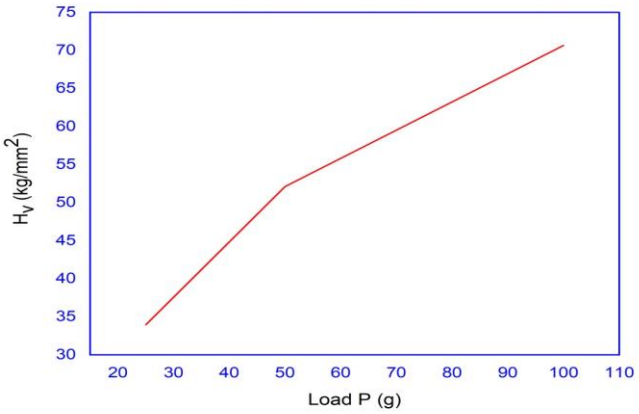


Fig. 6(a). Variation of microhardness number versus load P

A plot of micro hardness number versus load P for the grown SCHA crystal is shown in Fig.6 (a). From the graph it is found that as the load increases hardness number also increases and this indicates that the crystal exhibit Reverse Indentation Size Effect (RISE). SCHA crystal have higher hardness value of a crystal indicates that greater stress is required to form dislocation thus confirming that greater crystalline perfection is found in SCHA [33].

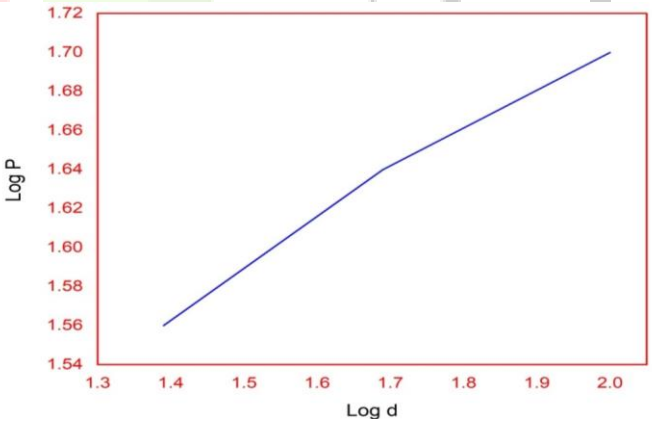


Fig. 6(b). Graph between Log P and Log d

Let P be the applied load in grams and d represent the diagonal length of the impression in millimeters. The work hardening coefficient, denoted by n, which quantifies the strength of the crystal is determined by analyzing the logarithmic plot of p verse d shown in Fig. 6(b). The work hardening index n of SCHA is found to be 2.8. According to Onitsch n should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials [34 - 37]. Since the work hardening index n of the crystal is above 1.6 the grown crystal is found to be as soft material.

The elastic stiffness constant ($C_{11}$) was calculated for the grown crystals using Wooster's empirical relation,

$$C_{11} = H_v^{7/4}$$

The variation of stiffness constant ($C_{11}$) with varied loads is shown in Fig. 6(c).

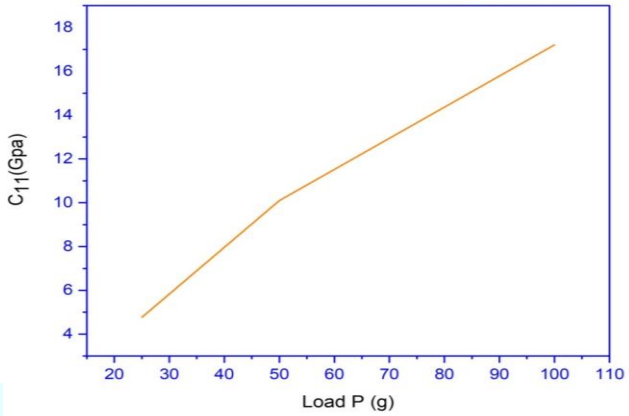


Fig. 6(c) Graph between Load p and $C_{11}$

The fracture toughness, denoted as Kc quantifies the amount of fracture stress that a material can with stand under uniform loading. This relationship is used to determine Kc. The variation of Fracture toughness with various loads is shown in Fig. 6(d). Graph between load P and brittleness index Bi as shown in Fig. 6(e) and Graph between load P and yield strength $\sigma_y$ as shown in Fig. 6(f).

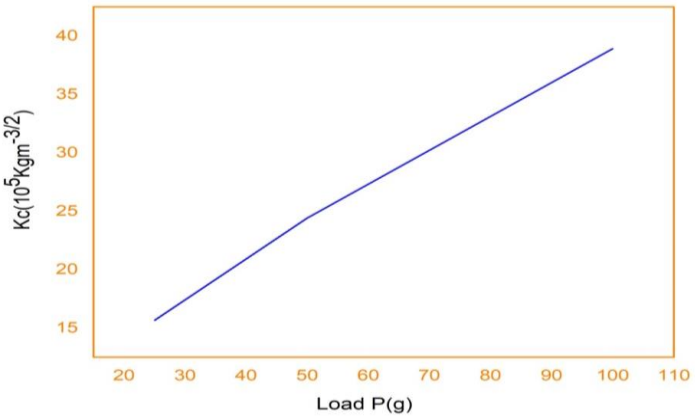


Fig. 6(d) Graph between Load P and Kc

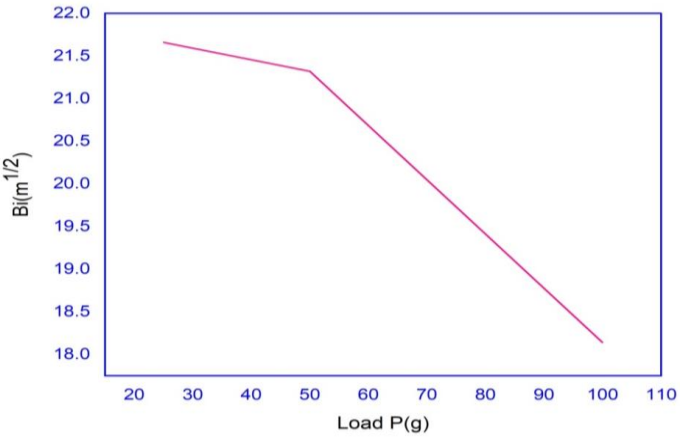


Fig. 6(e) Graph between Load P and Bi

The yield strength of the material can be found using the formula

$$\sigma_y = H\nu /3$$

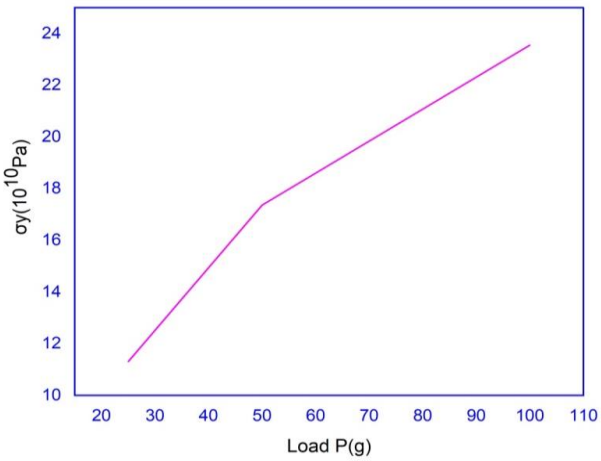


Fig. 6 (f). Graph between Load P and $\sigma_y$

Mechanical parameters value of SCHA determined for various loads are given in Table 1. The table shows that all the mechanical parameter value increases with load from 25g, 50g and 100g. Elastic stiffness constant ($C_{11}$) indicates the binding forces between the ions. Elastic stiffness increases with increase in load which indicates the tightness of bonding with neighbouring atoms. The high value of the stiffness constant indicates that the binding forces between atoms are quite strong. Fracture toughness values Kc determined from the measurements of crack length. It is one of the most important characteristics of any material for design applications. A material having high yield strength can withstand high stress without permanent deformation. The yield strength is an important property for engineering structural design and device fabrication.

Table 1. Mechanical parameter values of SCHA

| Mechanical parameters | Load for 25 g | Load for 50 g | Load for 100 g |
|---|---|---|---|
| Hardness Number $H_v$ ($Kg/mm^2$ ) | 33.95 | 52.1 | 70.85 |
| Elastic stiffness constant $C_{11}$(GPa) | 4.77 | 10.10 | 17.21 |
| Fracture toughness $K_C$ ($10^5$ $kg{\cdot}m^{-3/2}$) | 15.67 | 24.43 | 38.93 |
| Brittleness index Bi ($m^{1/2}$) | 21.66 | 21.32 | 18.14 |
| Yield Strength $\sigma_y$ ($10^{10}$ Pa) | 11.31 | 17.36 | 23.55 |

3.7. Second harmonic generation study

The nonlinear optical property of crystal was examined by the Kurtz and Perry powder technique. In this technique, the grown sample was grounded into fine microcrystalline powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser operated at the fundamental

wavelength 1064 nm with an input power of 1.1mJ and pulse width 10 ns and repetition rate 10Hz was allowed to pass through the sample cell. The amplitude of the SHG output was measured using photomultiplier and digitalizing oscilloscope assembly. The final output was displayed on a digital storage oscilloscope. The frequency conversion efficiency of the crystal was confirmed by the emission of green radiation from the sample. Here the conversion efficiency of SCHA sample is compared with standard reference potassium dihydrogen phosphate (KDP) sample. Comparison of these intensities reveals that the SCHA is 4.2 times higher than that of KDP. The results suggested that the SCHA crystal is useful for SHG device applications [38 - 44].

3.8. Thermal analysis

The thermal gravimetric analysis (TGA) of the compound was carried out between 0°C to 350°C at a heating rate of 10°C /min in the nitrogen atmosphere. The thermogram and the trace due to differential thermogram are illustrated in Fig. 7. There is an intense single stage weight loss between 200°C to 300°C.

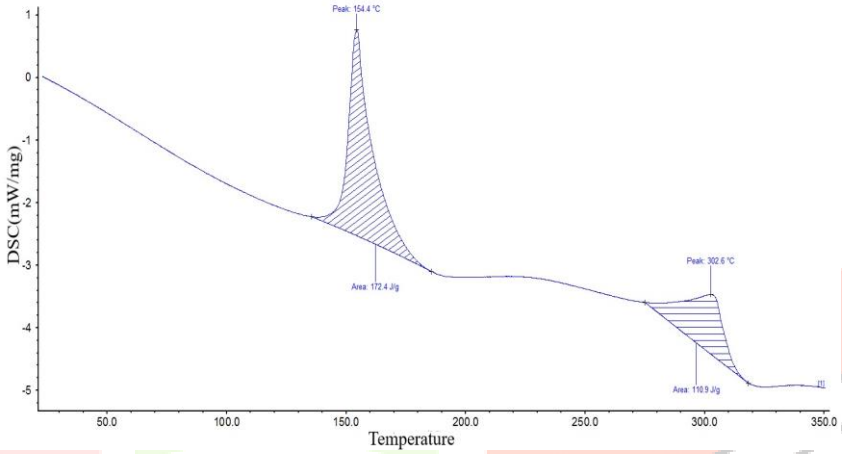


Fig. 7. DSC spectrum of SCHA

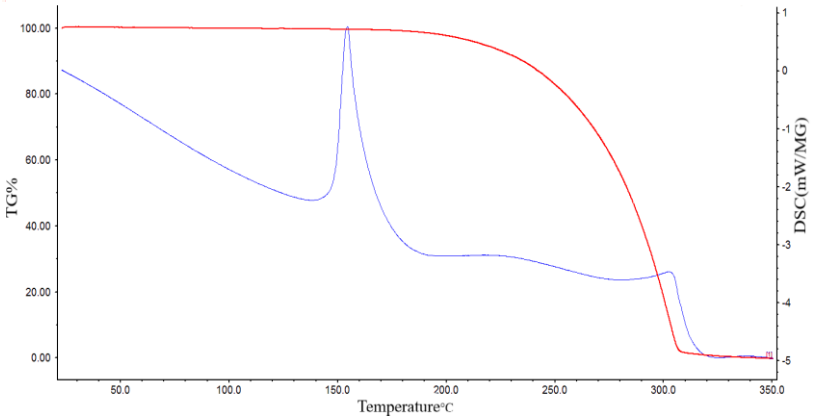


Fig. 8. TGA – DSC spectrum of SCHA

The DSC traces for both heating and cooling are shown in Fig. 8. The heating curve produces a sharp endothermic peak at 300°C due to melting [45 - 47]. The cooling curve produces the sharp intense exothers at 100°C illustrating crystallization of SCHA. The crystal disintegrates rapidly upon reaching temperatures between 200°C and 300°C, as indicated by the concurrent TG – DTG curve in Fig. 9.

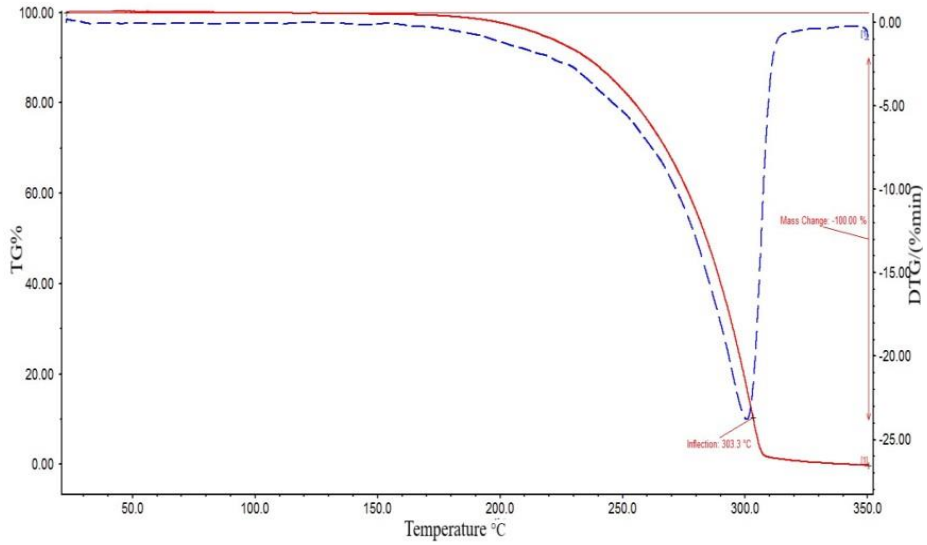


Fig. 9. TG – DTG spectrum of SCHA

## IV. CONCLUSION

The optically high quality colourless organic NLO single crystals of semicarbozidehydrochloride adipate have been grown by slow evaporation solution technique. The various characterization techniques have been employed to confirm the grown crystal such a single crystal XRD, FTIR, FT – Raman, UV – Vis – NIR, Fluorescence, mechanical studies, nonlinear optical property and thermal studies. Single crystal X-ray diffraction analyses confirm the grown crystal is orthorhombic and the space group is P. The FTIR and FT – Raman spectrum of the grown crystal confirm the presence of functional groups present in the compound. The UV – Vis – NIR transmission spectrum shows good transparency and the upper cut off wavelength is found to be 200 nm. The fluorescence spectrum shows the first sharp peak appears at a wavelength of 364 nm and it emits ultraviolet radiation. The second sharp peak appears at 532 nm and it emits green colour and the third small peak at 713 nm, it emits red colour. The microhardness study reveals that the hardness increases with increases the load. Mechanical parameter values are also calculated for the sample. The SHG efficiency of the grown crystal is about 4.2 times that of potassium dihydrogen orthophosphate. The thermal behaviour of the crystal was confirmed by TGA analysis. There is an endothermic peak at 300°C observed in the DTA curve and it corresponds to the melting point of the sample.

## V. ACKNOWLEDGEMENT

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REFERENCES

[1] M. Narayan Bhat and S. Dharmaprakash, J. Cryst. Growth, 236 (2002) 376 – 380.

[2] J. J. Rodrigues, L. Misoguti, F. D. Nunes, C. R. Mendonca and S. C. Zilo, Opt. Mater. 22 (2003) 235 – 240.

[3] K. Ambujam, S. Selvakumar, D. Prem Anand, G. Mohamed and P. Sagayaraj, Cryst. Res. Technol., 41 (2006) 671 – 677.

[4] G. Ramesh Kumar, S. Gokul Raj, R. Mohan and R. Jeyavel, Cryst. Growth and Des., 6 (2006) 1308 – 1310.

[5] J. Ramajothi, S. Dhanuskodi and K. Nagarajan, Cryst. Res. Technol., 39 (2004) 414 - 420.

[6] V. Kannan, R. B. Ganesh and P. Ramasamy, Cryst. Growth, Des.6 (2006) 1876 –1880.

[7] K. Ramya, N.T. Saraswathi and C. Ramachandra Raja, Opt and Laser Technol.,84 (2016) 102 - 106.

[8] P. Ilayabarathi and J. Chandrasekaran, Spectrochim. Acta A, 96 (2012) 684 - 689.

[9] P. Vasudevan, S. Sankar and S. Gokul Raj, Optik, 124 (2013) 4155 - 4158.

[10] P. Jayaprakash, M. Peer Mohamed, P. Krishnan, M. Nageshwari, G. Mani and M. Lydia Caroline, Physica B, 503 (2016) 25 - 31.

[11] N. Durairaj, S. Kalainathan and M.V. Krishnaiah, Mat. Chem. Phys., 181 (2016) 529 - 537.

[12] A. Suvitha, P.Vivek and P. Murugakoothan, Optik, 125 (2014) 141 - 145.

[13] A. Arunkumar and P. Ramasamy, Opt. Mat., 35 (2013) 1151 - 1156.

[14] S. G. Praveen, J. Binoy, J. T. T. Kumaran, C. Bansal, M. N. AudlineJini and V. S. Jayakumar, J. Mol. Struct., 1064 (2014) 81 – 87.

[15] Bismi Edwin and Joe. Hubert, Spectrochim. Acta A, 114 (2013) 633 – 641.

[16] T. Rajamani, S. Muthub and M. Karabacak, Spectrochim. Acta A, 108 (2013)186 – 196.

[17] P. Girija, S. Kumaravel, C. Vidya and P. M. Anbarasan, J. Adv. Sci., Eng., 3 (2017) 373 - 378.

[18] K. Uma, R. Manimekalai and G. Pasupathi, Int. J. Che. Mater. Reser., 3 (2015) 91- 99.

[19] C. Sudhakar and L. Jothi, Int. Res. J. Eng. and Tech., 9 (2022) 912 - 919.

[20] R. Anitha, S. Athimoolam, M. Gunasekaran and K. Anitha, J. Mol. Struct.,1076 (2014)115 – 125.

[21] Anandaraj Louis and Jothi Lakshmanan, J. Mine. and Mater. Charact., and Eng., 10 (2022)15 – 27.

[22] M. Manivannan and S. A. Martin Britto Dhas, J. Cryst. Growth, 455 (2016) 161 – 167.

[23] Himanshu Sharma, Bikash Kumar kalita, Debabrat Pathak and Bipul Sarma, Cryst. Growth and Des., 24 (2023) 17 - 51.

[24] P. Srinivasan, Y. Vidyalakshmi and R. Gopalakrishnan, Cryst. Growth and Des., 8 (2008) 2329 - 2334.

[25] K. Venkatesan , M. Kayalvizhi, L. Jothi and G. Vasuki J. Mol. Struct.,15 (2022) 132687.

[26] M. Senthil Pandian, N. Balamurugan, G. Bhagavannarayana and P. Ramasamy, J. Cryst. Growth, 310(2 008) 4143 - 4147.

[27] Kuriakose Jithin, P. Karuppasamy, M. Senthil Pandian and P. Ramasamy, J. Cryst. Growth, 652

(2025) 128025.

[28] M. N. Bhat and S. M. Dharmaprakash, J. Cryst, Growth, 236 (2002) 376 – 380.

[29] M. Lydia Caroline and S. Vasudevan, Mater. Lett., 62 (2008) 2245 – 2248.

[30] T. Uma Devi, N. Lawrence, R. Ramesh Babu and K. Ramamurthi, J. Cryst. Growth, 310 (2008) 116 – 123.

[31] D. Kalaiselvi and R. Jayavel, Appl. Phys., A, 107 (2012) 93 – 100.

[32] S. A. Martin Britto Dhas and S. Natarajan, Cryst. Res. Technol., 42(2008) 471 - 476.

[33] K. Deepa, N. Indumathi, S. Senthil and J. Madhavan, J. Engg. Sci., 2319 (2017) 26 – 30.

[34] R. Subhashini, D. Sathya, V. Sivashankar, P. S. Latha Mageswari and S. Arjunan, Opt. Mater.,62 (2016) 357 – 365.

[35] K. Meera, R. Muralidharan, A. K.Tripathi and P. Ramasamy, J. Cryst. Growth, 263 (2004) 524 – 553.

[36] D. Kalaiselvi and R. Jayavel, Appl. Phys., A, 107(2012) 93 – 100.

[37] M. R. Suresh kumar, H. J. Ravindra, A. Jayarama and S. M. Dharmaprakash, J. Cryst. Growth, 286 (2006) 451 - 456.

[38] Harsh Yadav, Nidhi Tyag and Binay Kumar, Cryst. Growth Des., 15(2015) 4908 - 4917.

[39] S. Senthil, S. Pari, P. Sagayaraj, J. Madhavan, Phys., B, 404 (2009) 1655 – 1660.

[40] R. Ramesh Babu, N. Vijayan, R. Gopalakrishnan and P. Ramasamy, J. Cryst. Growth, 240 (2002) 545 - 548.

[41] S. S. Hussaini, N. R. Dhumane, G. Rabbani, P. Karmuse, V. G. Dongre and M. D. Shirsat, Cryst. Res. Technol., 42 (2007) 1110 - 1119.

[42] K. Vasantha and S. Dhanuskodi, J.Cryst. Growth, 263(2004) 466 – 472.

[43] P. Rajesh and P. Ramasamy, J.Cryst. Growth, 311(2009) 3491- 3497.

[44] Sana Islam, Imran Aslam, Tariq Mahmood and M. Hassan Farooq, J.Cryst. Growth, 652(2025) 128017.

[45] Yuui Yokota, Yuji Ohashi, Yasuhiro Shoji and Akira Yoshikawa J.Cryst. Growth, 652(2025) 128013.

[46] S. Akilandeswari and L. Jothi, J. Mine. and Mater. Charact., and Eng., 9 (2021) 75 - 89.

[47] L. Jothi and K. Ramamurthi Ind. J. Sci. Technol., 4 (2011) 666 - 669.