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Growth and Characterization of Adipic Acid Doped Single Crystal

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ABSTRACT

Organic NLO materials have been used for a large number of technological applications in laser sources. In the present work thiourea crystal grown from aqueous solution with Adipic acid which has an organic nonlinear optical material is employed. The cell parameters of the grown crystal were determined by single crystal X-ray diffraction analysis. The optical properties of the crystal were examined by UV- Vis analysis. Fourier transform infrared spectroscopy (FTIR) is used to confirm the functional group of the crystal. The second harmonic generation (SHG) was tested by Kurtz Perry powder test. The Thermal stability and mechanical properties of the grown crystal were confirmed by TGA/DTA and vicker's hardness analysis.

Key Words: SXRD, SHG, TGA/DTA

INTRODUCTION

The field of crystal growth is enriched by organic NLO crystals due to their high optical nonlinearities and quick response in the electro-optic effect compared to the inorganic analogues [1–5]. Advanced Technology uses materials with high second order harmonic generation efficiencies and transparent characteristic in the region of UV-Visible and IR region. Molecular flexibility of organic materials is an added advantage to enhance the nonlinear optical (NLO) properties in a desired manner. Adipic acid has good optical, thermal and mechanical properties [6]. The stability of the crystal is improved by adipic acid as the dopant with thourea. Thourea is a well-known organic NLO material, having good electro-optic properties and is favoured for its crystal growth in a bulk size suitable for device applications [7].

CRYSTAL GROWTH

Thiourea and Adipic acid were used for the growth of single crystals. Both the compounds in Analytical reagent grade (AR) sample and double distilled water has been used as solvent by solution evaporation method. The equimolar adipic acid and thourea supersaturated solution were blended well to attain the homogenous solution. The solution was kept for evaporation in closed manner. The purity of crystal was elevated by successive recrystallization process which was free from macro defects by self-nucleation of saturated solution. Single crystals of Adipic acid doped Thourea have been harvested within 20 days were shown in figure 1.

RESULTS AND DISCUSSION

XRD Analysis

The cell dimensions of the adipic acid doped thiourea crystal were obtained by single crystal X-Ray diffraction analysis. The crystal system was found to be a orthorhombic system. The lattice parameter values were found to be: a = 5.46 Å, b= 7.59Å, c = 8.49Å and volume 352 $Å^3$.The cell parameters were good agreement with reported values of pure adipic acid and Thiourea [8-9].

FTIR Analysis

Adipic acid doped thiourea crystal was characterized by FTIR spectroscopy in order to identify the functional groups. The measurement was done with KBr pellet method for the wavelength range 400-4000cm^{-1} . The spectra as shown in figure 2 and assignments are tabulated in Table 1[9-10].

Optical Studies

The transmission spectrum of Adipic acid doped Thiourea crystal are recorded using UV-Vis spectrometer (BERKIN ELMER LAMBDA 35) in the wavelength range between

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100nm and 1100nm are shown in figure 3. The absorbance is not enrolled in the wavelength range starting from 358nm to 876nm and this is an advantage for materials having NLO properties. The sharp fall of the transmittance was observed in 358nm which indicates the single crystal have the transmission in UV region and their no transmission in the visible region.

SHG Efficiency

The NLO property of adipic acid doped thiourea single crystal was performed by Kurtz Perry powder technique[11]. The crystal was grained into powder and densely packed in the microcapillary tube of uniform diameter. Quanta-Ray Spectra physics ND:YAG laser producing pulses with a width of 8ns and a repetition rate of 10Hz was used. The laser was focused on falling on the powder sample. SHG was confirmed by the emission of green radiation (532nm) and the optical signal was controlled by a photomultiplier tube (PMT) and converted into voltage output in CRO [12-13]. The powder SHG efficiency of the grown crystal was found to be 0.5 times that of the standard KDP crystal.

Microhardness Measurement

The mechanical properties of the grown single crystals were obtained by Vicker's hardness test. It is calculated by using the formula and graph drawn between load and Hv as shown in Fig.4.

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

Hv = Vickers hardness number, P = load in kg , d = arithmetic mean of the two diagonals

From the Fig.4, Vickers hardness number Hv increases with an increase in the load. The Mayer's index number was calculated from the Mayer's law, which relates the load and indentation diagonal length

$$P = kd^n$$

$$\log P = \log k + n\log d$$

Where k is the material constant and n is the Mayer's index (or work-hardening coefficient). The slope of the plot of log P versus log d will give the work hardening index (n) which is found to be 2.5. The grown crystal Adipic acid doped Thiourea is confirmed to have a large amount of mechanical strength(σ_y) which is better for device fabrications. The elastic stiffness constant (C_{11}) and Yield strength were calculated by Wooster's empirical relation [14] as shown in Table 2.

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

Yield strength is a point at which material exceeds the elastic limit and will not return to its original shape or length if the stress is removed. Yield strength is one of the important properties for device fabrication and can be calculated by the relation,

$$\sigma_y = Hv / 3$$

Thermal Analysis

The thermal stability of the grown single crystal were carried out by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) at heating 20ºC/min in air as shown in Fig 6. [15]. The TG curves shows that upto the melting point there is no weight loss. The weight loss happen on crystal at 160ºC to 290 ºC. The DTA curve shows that doped crystal was thermally stable and suitable for device applications. It is observed that the crystal shows the first endothermic peak at 159 ºC and the exothermic peak at 378 ºC which correspond to the melting point and decomposition point of the sample.

CONCLUSION

The Adipic acid doped Thiourea crystals were grown by a slow evaporation technique. The FTIR spectrum confirms the presence of functional group for the grown crystal. The UV-Vis spectral analysis shows the absorption and transmission of the crystal. In TGA curve, there is no weight loss up to the melting point of the crystal. The Second harmonic generations were confirmed by the emission of green radiation. It is a potential material for frequency conversion. The Vicker's microhardness test was carried out for the grown crystal and the crystal belongs to hard material from the work hardening coefficient value.

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REFERENCES

1. J. Zyss, "*Molecular Nonlinear Optics: Materials, Physics and Devices*, 1993,Academic Press, *New York*.
2. F. Agullo -Lopez, J.M. Cabrera, F. Agullo -Rueda, *Electrooptics: Phenomena,Materials and Applications*", 1994, Academic Press, *New York*.
3. V.A. Russel, C.C. Evans, W. Li, M.D. *Ward, Science,* (1997), 276, 575.
4. J. Zyss, *J. Phys. D: Appl. Phys*., (1993), 26, 8198.
5. G.R.Desiraju, "*Crystal Engineering, The Design of Organic Solids"*, 1989, *Elsevier,New York,* 1989.
6. Shanthi A, Krishnan C, Selvarajan P, "*Growth and characterization of a single crystal of Urea Adipic acid (UAA)--a third order nonlinear optical material*", (2014), Spectrachemica Acta part A. 122, 521–528.
7. B. Ravi, A. Jegatheesan , Neelakanda Prasad, C. Sadeesh Kumar , G. Rajarajan , "*Optical and Conductivity Analysis of Thiourea Single Crystals",* (2014)*Rasayan J. chem*. Vol. 7, No.3,

287 – 294.
8. Linda Williams-seton ,Roger ,J Davey, Harvey F. liberman, Robin G.Pritchard, "*Disorder and twinning in molecular crystals: Impurity-induced effects in adipic acid*",(2000), *J . Pharamaceutical Sciences*. 89, 346-354.
9. Sandhya Ravi, S. Chenthamarai, "*Growth and Characterization of Single Crystals of Thiourea Based .Compounds"*, 2014,Indian J.Sci.Res. 9(1), 051-057, 2014
10. Masako Suzuki and Takehiko Shimanouchi, *Infrared and Raman Spectra of Adipic acid Crystal*, (1969), Journal of Molecular spectroscopy 29, 415-425.
11. Kurtz S.K, Perry TT., "*A powder technique for the evaluation of nonlinear optical materials",* (1968), *J Appl Phys*.39, pp 3798–3813.
12. Raja, R., Seshadri, , Saravanan, R.R, "*Crystal growth , spectral, thermal and optical properties of an organic single crystals – Dye doped hippuric acid*", (2014), Optik 125, 916-919.
13. Raja R., Seshadri S., Gnanasambantham, Saravanan, R.R, "*Crystal growth and properties of NLO optical crystals Butlated Hydroxy Toluene (BHT)*", (2014), *Spectrachemica Acta part A*.138, 13-20.
14. Ruban Kumar A., Kalainathan S, (2010), "*Microhardness studies on calcium hydrogen phosphate (brushite) crystals*", (2010), *Mater. Res.Bull*. 45, pp 1664.
15. Shanmugam G, Thirupugalmani K, Rakhikrishna R, Philip J, Brahadeeswaran S., "*Thermo physical, mechanical and dielectric studies on piperidinium p-hydroxybenzoate*", (2013), *J Therm Anal Calorim*., 114, pp 1245–54.

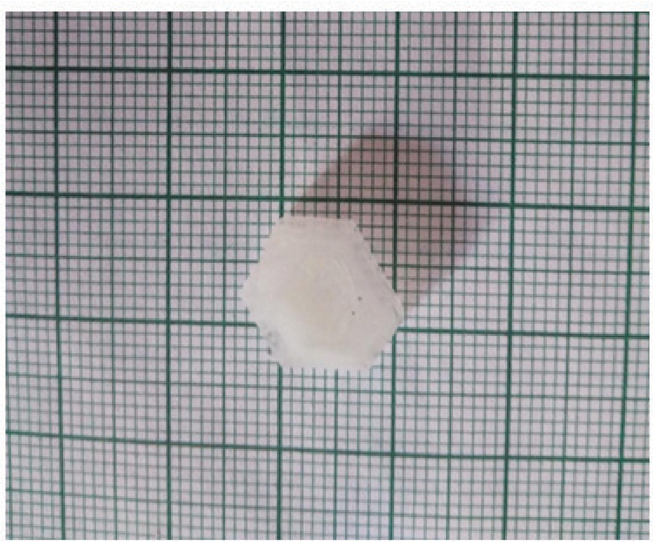

Figure 1: Grown crystal of TUAP crystal Single crystal.

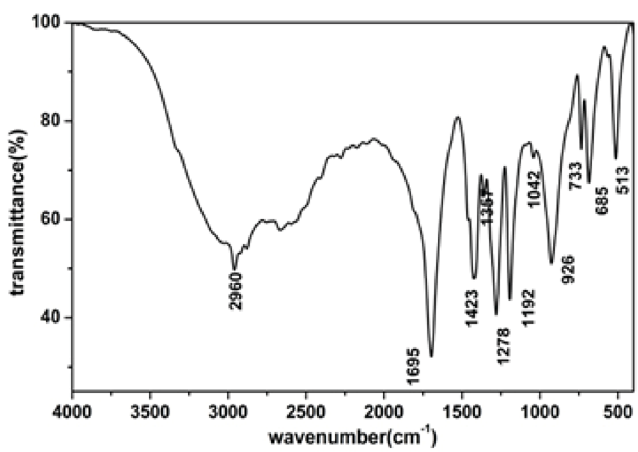

Figure 2: FTIR spectrum of TUAP Single crystal.

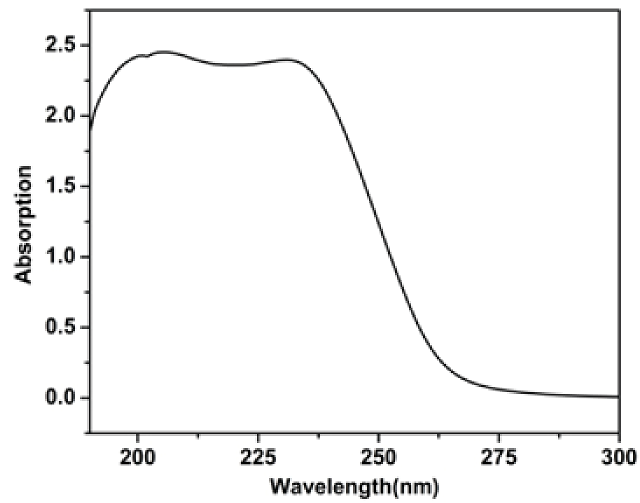

Figure 3: Transmission spectrum of TUAP single crystal.

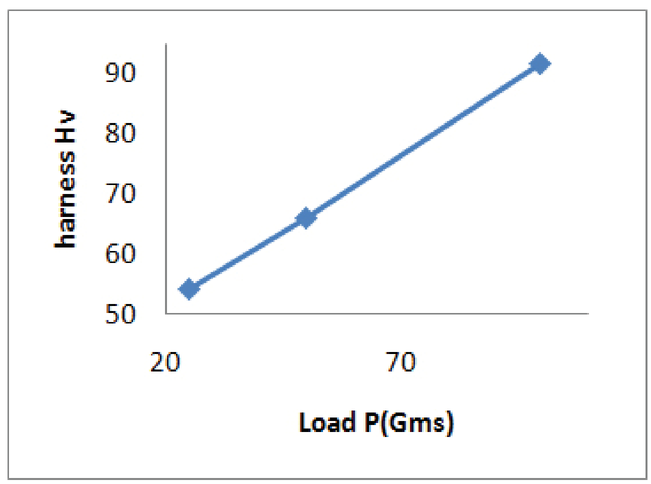

Figure 4: Hardness behavior of TUAP single crystal.

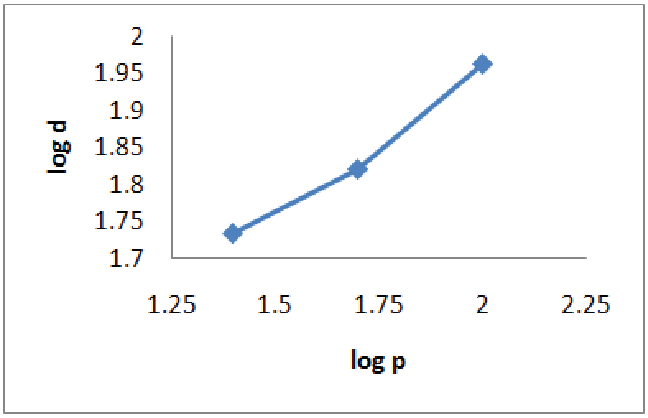

Figure 5: log p VS log d graph of TUAP crystal.

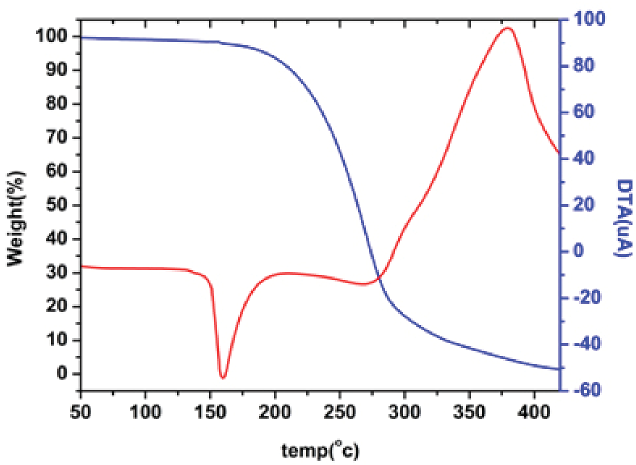

Figure 6: TGA/DTA graph of TUAP single crystal.

Table 1: FTIR Assignments

Wavenumber (cm^{-1})	Band Assignments
2960	CH Stretching
1695	C=O Stretching
1459	C-N asymmetric stretching
1423	C=S` asymmetri stretching
1357	CH_2 Bending
1278	C=O Stretching
1192	CH_2 Bending
1042	C-C Stretching
926	C-C Stretching
733	C=S symmetric stretching
685	N-C-S asymmetric bending

Table 2: Elastic Stiffness and Yield

Load (P) g	Hv (kg/mm²)	C_{11} (x10 $^{-3}$M Pa)	σ_y (M Pa)
25	54.15	10.80	180.5
50	65.95	15.26	219.83
100	91.7	27.17	305.67