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Determination of Induction period,Interfacial energy, Nucleation parameters Thermal studies and SHG efficiency of [(E)-benzylideneamino] thiourea

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Abstract

The semi organic Non-linear crystal of [(E)-benzylideneamino] thiourea was prepared by adopting slow evaporation solution growth technique. The, induction period, interfacial energy and nucleation parameters of the material was determined for the solvents methanol,1:1 methanol and 1:2 methanol. The resulting crystals were subjected to UV-Visible spectral study to determine its optical transparency, FT-IR Spectral study to determine its purity. Thermal studies support the thermal stability of the material. Further the material was found to be about 5.1 time SHG efficient than that of potassium dehydrogenate ortho phosphate. These studies reveals the application oriented properties of the material-[(E)-benzylideneamino] thiourea.

Keywords: Solution growth, slow evaporation technique, spectral characterization, thermal analysis.

Introduction

In recent years, intense research work has been carried out to identify a special variety of thermally stable optical material. Generally semi-organic crystals are more stable; particularly this - [(E)-benzylideneamino] thiourea crystals has an optical transparency. The slow evaporation solution growth technique (SESGT) is an important technique because large size, stable, optical crystals are being grown by this technique[1-6]. The application oriented grown crystal is applied in inert area of optical communication, computing and information process. A major drawback of crystalline organic optical crystal is the difficulty in growing large, optical quality crystals also the often fragile nature of these crystals makes them difficult to process. The inherent limitation on the maximum nonlinearity in inorganic materials and the moderate success in growing device grade organic crystals has made scientists to adopt alternate strategies. The obvious one was to develop hybrid inorganic - organic materials with some advantages. Therefore in the present studies, We report on the induction period, interfacial energy and nucleation parameters, thermal studies and SHG efficiency of [(E)-benzylideneamino] thiourea crystals by slow evaporation solution growth technique (SESGT). The nucleation parameters for solution grown [(E)-benzylideneamino] thiourea were determined using the interfacial tension and reported for the first time.

The Induction period, Interfacial energy and nucleation parameters of [(E)-benzylideneamino] thiourea in pure methanol, 1:1 methanol and 1:2 methanols as solvent were determined. The grown crystal was characterized by UV for the optical property, the functional group are characterized by FT-IR, thermal properties are characterized by TGA and DSC analysis and NLO studies for SHG efficiency[7-12].

Material and Methods

The semi organic crystal of [(E)-benzylideneamino] thiourea was prepared by the slow evaporation solution growth technique (SESGT)[13-17]. By taking appropriate amount of Thiosemicarbazide of a hot solution in methanol, a solution of benzaldehyde in methanol was added drop wise during 30 minuts. The content was fitted in reflux condenser with constant stirring maintain this condition up to 4 hrs. Then filtered the content, concentrate it to half the volume. After a slow evaporation of the concentrate at room temperature. Crystals were collected, to improve the purity of the crystal washed with ethanol (at least 5 times) thoroughly.

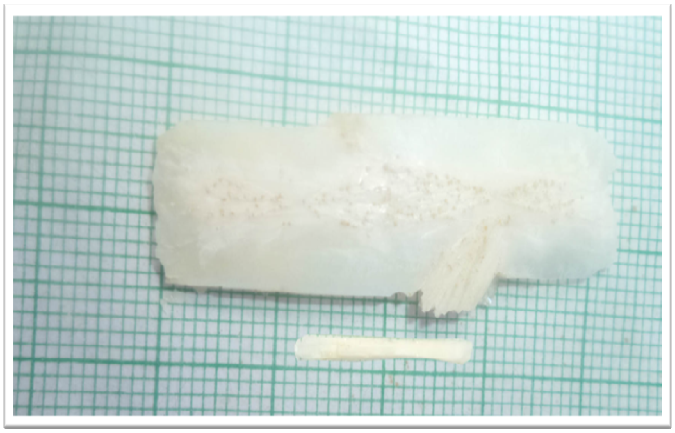

Figure-1
Crystals of [(E)-benzylideneamino] thiourea

Induction periods and Interfacial energies

There are several methods of measuring the induction period depending upon the solubility of the materials[18]. Here the visual observation method was followed. Solutions of [(E)-benzylideneamino] thiourea in methanol at different supersaturation values were prepared and subjected to systematic slow evaporation. The time period that elapses between the achievement of supersaturation and appearance of visual nuclei is taken as the induction period (t). Several trial runs were performed to minimize the error. Experiments were repeated for supersaturation (s) like 1.15, 1.17, 1.20 and 1.25at two different temperatures. From the results obtained a plot of lnt against $1/(\ln s)^2$ is drawn and is shown in figure2. The interfacial tension was calculated from the slope of the curves using the equation $\ln t = \ln A + 16\pi r^3 V^2 N / 3RT(\ln s)^2$

Where A is a constant related to the pre-exponential factor of the nucleation rate expression. V is the molar volume, N is the Avogadro number and R is the gas constant. The factor $16\pi r^3$ in the above equation refers to the spherical nuclei. The interfacial tension between the [(E)-benzylideneamino] thiourea and methanol is calculated by measuring the slope value of the curve obtained at the two temperatures.

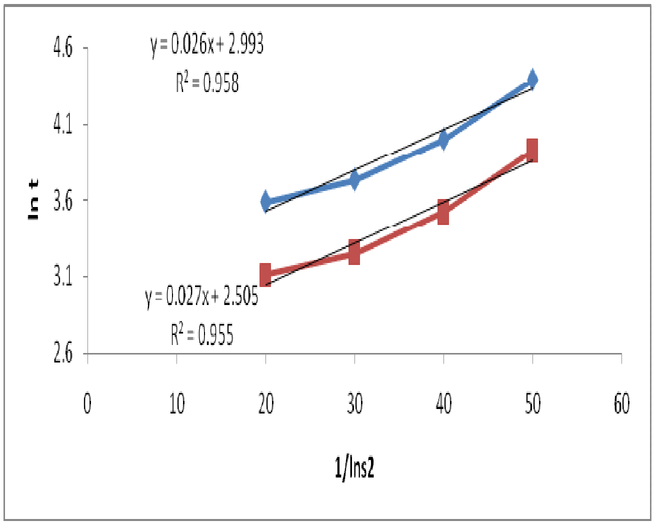

Figure-2
A plot of lnt vs $(\ln s)^2$ for [(E)-benzylideneamino] thiourea grown from Methanol at 308 and 313K

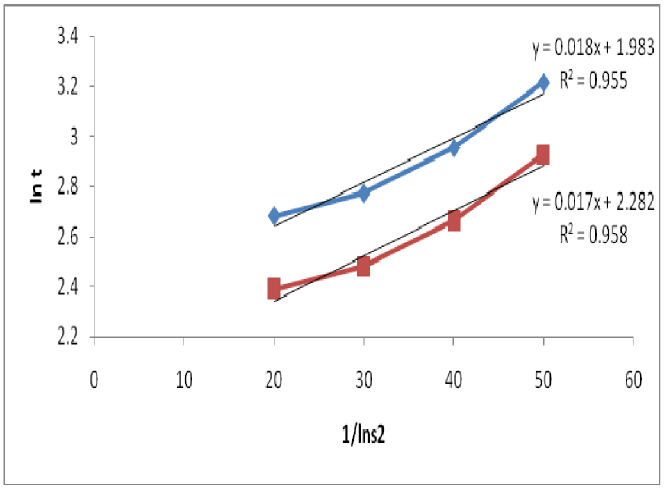

Figure-3
A plot of ln t vs $1/(\ln s)^2$ for[(E)-benzylideneamino] thiourea grown from Methanol 1:1 at 308 and 313K

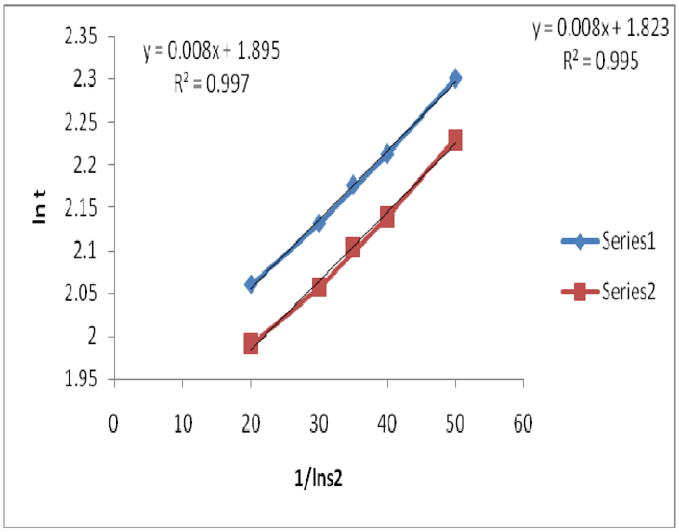

Figure-4
A plot of ln t vs $1/(\ln s)^2$ for [(E)-benzylideneamino] thiourea grown from Methanol 1:2 at 308 and 313K

Similar experiments were made in the case of 1:1 methanol and 1:2 methanol solvents also. From the results obtained .plots of ln t against $1/(\ln s)^2$ are drawn and shown in figures 3 and 4.The effect of solvent and temperature on interfacial tension is presented in table 1.

Table-1
Effect of temperature and solvent on interfacial tension

Solvent	Temperature/K	Slope value	Interfaciel tension/mj/m^2 ×10^{-13}
Pure methanol	308	0.0267	2.0406
	313	0.0270	2.1433
1:1 methanol	308	0.0178	1.8607
	313	0.0180	1.9372
1:2 methanol	308	0.0080	1.7328
	313	0.0080	1.7629

According to the classical homogeneous nucleation theory, the Gibbs free energy required to form [(E)-benzylideneamino] thiourea nucleus is given by

$\Delta G = (4/3)\pi r^3\ \Delta G_{v+} 4\pi r^2 \gamma$ (2)

Where ΔG_v is the Gibbs free energy change per unit volume, r is radius of the nucleus. At the critical state, the formation obeys the condition that $d(\Delta G)/dr = 0$.Hence the radius of the critical nucleus is expressed as

$r^* = -2\gamma/\ \Delta G_v$

where, $\Delta G_v\ = --kt\ \ln s/v$ (3)

Where v is the molar volume, and S=C/C*.C actual concentration and C*- equilibrium concentration

Hence $r^* = 2v\gamma/KT\ \ln s$ (4)

The critical Gibbs free energy is given by

$\Delta G^* = 16\pi r^2 v^2/\ \Delta G^2$ (5)

The number of molecules in the critical nucleus is expressed as

$i^* = 4\pi (r^*)^3/3v$ (6)

Therefore, using the interfacial tension value. the radius, of the critical nuclei (r*), the Gibbs free energy change for the formation of a critical nucleus (ΔG^*) and the number of molecules (i*) were calculated at different temperature for [(E)-benzylideneamino] thiourea in methanol and presented in Table 1.

It was noted that with the increase in super saturation, the Gibbs free energy change for the formation of a critical nucleus (ΔG^*) decreases with radius(r*).This favours the easy formation of nucleation in methanol at higher super saturations.

Similar type of calculations used to calculate the nucleation parameters of [(E)-benzylideneamino] thiourea in 1:1 and 1:2 methanol the values are given in Table 3 and 4 respectively.

The surface tension of the solvent methanol is in increasing order with decreasing concentration. The effect of surface tension on interfacial tension is given in table 7. The interfacial tension between the pure methanol, 1:1 methanol and 1:2 methanol is also in decreasing order. The effect of viscosity of solvents on interfacial tension is given in table 6. As viscosity increases the interfacial tension decreases. The effect of density of solvents on interfacial tension is presented in table 7. As density increases the interfacial tension decreases.

Table-2

Nucleation parameters of[(E)-benzylideneamino] thiourea crystal in methanol

Super saturation ratio S=C/C*	**308 K**			**313 K**		
	r*/m X 10^{12}	**ΔG* X 10^{12}**	**i* X 10^{38}**	**r*/m X 10^{12}**	**ΔG* X 10^{12}**	**i* X 10^{38}**
1.15	7.7900	6.2216	3.9584	8.0512	6.9801	4.3700
1.17	6.9676	4.9773	2.8324	7.2012	5.5841	3.1269
1.20	6.0341	3.7330	1.8397	6.2364	4.1881	2.0310
1.25	4.9268	2.4886	1.0014	5.0920	2.7920	1.1055

Table-3

Nucleation parameters of [(E)-benzylideneamino] thiourea crystal in 1:1methanol

Super saturation ratio S=C/C*	**308 K**			**313 K**		
	r*/m X 10^{12}	**ΔG* X 10^{12}**	**i* X 10^{38}**	**r*/m X 10^{12}**	**ΔG* X 10^{12}**	**i* X 10^{38}**
1.15	7.1031	4.7166	3.0008	7.2771	5.1542	3.2269
1.17	6.3532	3.7733	2.1472	6.5088	4.1233	2.3089
1.20	5.5020	2.8300	1.3946	5.6368	3.0925	1.4997
1.25	4.4924	1.8866	0.7591	4.6024	2.0617	0.8163

Table-4

Nucleation parameters of [(E)-benzylideneamino] thiourea crystal in 1:2 methanol

Super saturation ratio S=C/C*	**308 K**			**313 K**		
	r*/m X 10^{12}	**ΔG* X 10^{12}**	**i* X 10^{38}**	**r*/m X 10^{12}**	**ΔG* X 10^{12}**	**i* X 10^{38}**
1.15	6.6149	3.8093	2.4236	6.6224	3.8844	2.4319
1.17	5.9165	3.0475	1.7342	5.9232	3.1075	1.7401
1.20	5.1238	2.2856	1.1264	5.1297	2.3306	1.1302
1.25	4.1836	1.5237	0.6131	4.1883	1.5538	0.6152

Table-5
Effect of surface tension of solvents on interfacial tension

Solvent	surface tension, , r/N m	interfacial tension at 35’c, /mJ/m^2 ×10^{-13}
Pure methanol	0.02212	2.0406
1:1 methanol	0.02561	1.8607
1:2 methanol	0.02649	1.7328

Table-6
Effect of viscosity of solvents on interfacial tension

Solvent	Viscosity,m.pa.s	interfacial tension at 35’c /mJ/m^2 ×10^{-13}
Pure methanol	0.544	2.0406
1:1 methanol	1.271	1.8607
1:2 methanol	1.246	1.7328

Table-7
Effect of density of solvents on interfacial tension

Solvent	Density,Kg/ l	interfacial tension at 35’c /mJ/m^2 ×10^{-13}
Pure methanol	0.7893	2.0406
1:1 methanol	0.9139	1.8607
1:2 methanol	0.9455	1.7328

Results and Discussion

UV Visible Spectral studies: UV-Visible Spectral study is very useful technique to determine the optical properties and transparency of a substance[19-23].The UV-Visible spectrum of [(E)-benzylideneamino] thiourea crystal was recorded using Lambda 25 spectrometer is shown in figure-5.

This spectrum shows the characteristic absorption around 325-425nm which is assigned to a substituted benzene with $–NH_2$ group and $–SO_3H$ group. This spectrum also confirms the aromatic nature of grown crystal. The recorded UV-Visible spectrum proves the highly transparent nature of the material between 425-800nm. This confirms the characteristic property of [(E)-benzylideneamino] thiourea, which is suitable for optical application.

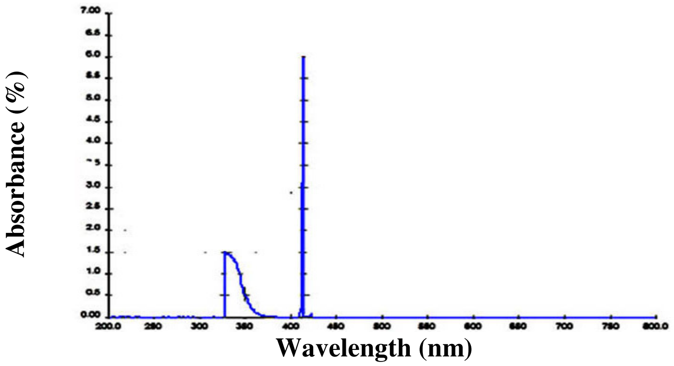

Figure-5
UV-Visible Spectrum of [(E)-benzylideneamino] thiourea

FT-IR Spectral analysis: Functional groups present in the sample were analyzed using Fourier Transform Infrared spectrum[24-28]. The spectrum was recorded using AVTAR370 DTGS FT-IR spectrometer in the wave number range from 400-4000cm^{-1} with KBr pellet. The Fourier Infra-red spectrum (FT-IR) of the grown crystal is shown in figure-6. The observed and their corresponding group identification is given in table-8.The band obtained at 1590cm^{-1} is due to the formation of the imine group between benzaldehyde and thiosemicarbazide. Due to the C=N and N-N stretching vibration the peaks observed at below 1500 cm^{-1}. The peak observed at 1159.23cm^{-1} shows C=S stretching vibration. As expected the peak corresponds to aromatic C-H was observed at 1298cm^{-1}. There is no peak observed at 2720 cm^{-1}confirms the aldehyde functional group in [(E)-benzylideneamino] thiourea .

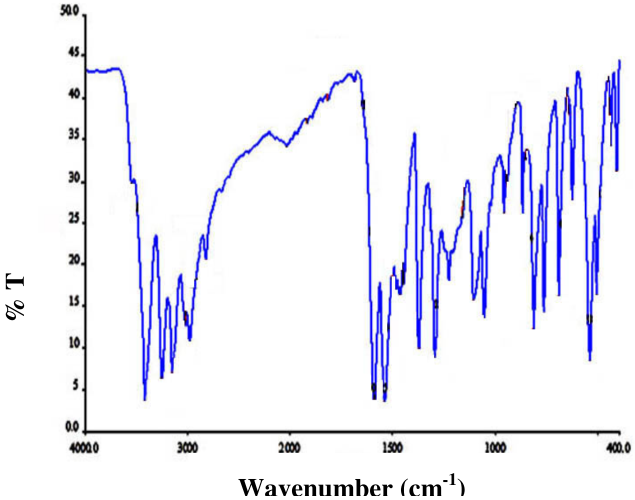

Figure-6
FT-IR Spectrum of [(E)-benzylideneamino] thiourea

Table-8
The observed and their corresponding group identification

S.No	Frequency cm^{-1}	Group identification
1	1590	C=N imine group
2	1500	N-N Stretching
3	1159	C=S Stretching
4	1298	Aromatic C-H
5	1107	NH_2 rocking

Thermal analysis: Thermal study of [(E)-benzylideneamino] thiourea was analyzed using SDT Q 600V 20.9 BUILD20 instrument between the temperature o0C to 600^0 Cat a heating rate of 10^{0}C/minutes under nitrogen atmosphere. The thermal analysis is a very useful technique in the characterization and thermal stability of the crystal[29-31]. The thermograme of [(E)-benzylideneamino] thiourea shown in figure-7. The sample weight is 10.9750 mg sample was taken for the measurement The Thermogram shows the endothermic peak at 153.50^{o}C. Further shows the grown crystal has crystalline nature and thermal stability. The grown crystal begins to attain an endothermic transition and begins decompose. The sharpness of this endothermic peak shows the good degree of crystallinity and purity. In TGA there are three weight losses noted in the thermo gram First one is due to expulsion of water present in the crystal. The second and third major weight loss is observed just above 200^{o}C and 300^{o}C.

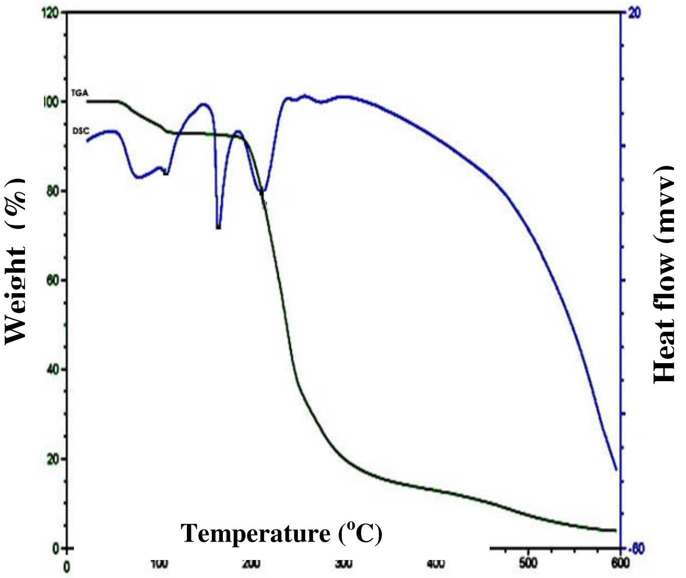

Figure-7
Thermogram of – [(E)-benzylideneamino] thiourea

Nonlinear optical studies: Kurts and perry second harmonic generation (SHG) tests[32] was performed to determine the NLO efficiency of [(E)-benzylideneamino] thiourea crystal. The grown crystal was powdered with a uniform particle size and packed in a micro capillary of uniform bore and was illuminated using spectra physics quanta ray DHS2.Nd:YAG laser is used to test second harmonic generation (SHG) of grown crystal, The SHG efficiency obtained for [(E)-benzylideneamino] thiourea is about 5.1 times that of potassium dihydrogen orthophosphate crystal.

Conclusion

[(E)-benzylideneamino] thiourea was prepared by using benzaldehyde and Thiosemicarbazide in methanol solution by adopting standard procedure. The crystal was grown by slow evaporation solution growth technique (SESGT). The UV-Visible spectrum reveals that the grown crystal is transparent in the wavelength region The presence of benzaldehyde group is identified by FT-IR Spectral analysis**.** Thermal stability of the crystal was confirmed by TGA/DSC studies.The NLO test confirms the SHG efficiency of [(E)-benzylideneamino] thiourea .

Reference

1. Anbusrinivasan P., Pandian G.V., Determination of Nucleation Temperature, metestablezonewidth spectral analysis of sulphanilic acid grown from Ethanol-Water as growth medium, *Ultra chemistry,* **8(1),** 83-90 **(2012)**
2. RamachandraRaja C., Ramamoorthi K. and Manimekalai R., Growth and spectroscopic characterization of ethylene diamine tetra acetic acid (EDTA) doped Zinc sulphatehepta hydrate-A semi organic NLO material, *Spectrochimica Acta Part A.,* **99,** 23-26 **(2012)**
3. Madhurambal G., Ramasamy P., Anbusrinivasan P., Vasudevan G., Kavitha S., Majumdar S.C., Growth and characterization studies of 2- bromo-4''-Chloro-acetophenone (BCAP) crystals, *J Therm Anal calorim*, **94,** 59-62 **(2008)**
4. Vasudevan G., Anbusrinivasan P., Madhurambal G. and Mojumdar S.C., Thermal analysis effect of dopants Spectral characterization and growth aspect of KAP crystals, *J Therm Anal Calorim,* **(96)** 99-102 **(2009)**
5. Ramalingam S., Anbusrinivasan P., Periandy S:FT-IR and FT-Raman Spectral Investigation, Computed IR-Intensity and Raman activity analysis and frequency estimation analysis on 4-chloro-2-bromoacetophenone was – HF and DFT calculations; *Spectrochimica Acta part A,* **(78),** 826-834 **(2011)**
6. Manivannan S., Danuskodi S. Growth and characterization of a new organic nonlinear crystals: Semicarbazone of N-dimethylaminebenzaldehyde, *J.Crystal growth,* **257,** 305-308 **(2003)**
7. Yun-zhang, Yonggangwang, Yunxiache, Jiminezheng Growth and properties of two new organic nonlinear optical crystals; Hydroxyethylammonium-l-tartrate monohydrate and Hydroxyethylammonium-o-tartratemonohydrate, *J crystal growth,* **299,** 120-124 **(2007)**
8. Rajasekaran M., Anbusrinivasan P., Mojumdar S.C., Growth, Spectral and thermal characterization of 8-hydroxyquinoline, *J. Therm calorim,* **100,** 827-830 **(2010)**
9. Sankaranarayanan K., Ramasamy P., Unidirectional crystallization of large diameter benzophenone single crystal from solution at ambient temperature, *J crystal growth,* **292,** 445-448 **(2006)**
10. Arulchakkaravarthi A., Jayavel P., santhanaragavan P., Ramasamy P., Growth of organic molecular single crystal trans-stilbene by selective self-seeding from vertical Bridgman technique, *J. cryst Growth,* **(234),** 159-163 **(2002)**
11. Subashini A., Bhavannarayana G. and Ramamurthi K., Investigation on growth and crystalline perfection of an organic Schiff base material:4-chloro-4''

bromobenzylidene aniline, *Spectrochimica Acta part A.,* **96**, 716-722 **(2012)**

12. Srinivasan P., Gunasekaran M., Ganagasekaran T., Gobalakrishnan R., Ramasamy P. 2, 4, 6-trinitrophenol (TNP); an organic material for nonlinear optical applications, *J. Cryst Growth,* **(289)**, 639-646 **(2006)**

13. Wiliredo Hermandeza and Juanpaz, Abraham Vaisberg, Evgenia Spodine, Rainer Richter and lothar Beyer, Synthesis, Characterization and in Vitro Cytotoxic Activities of Benzaldehyde Thiosemicarbazone Derivatives and their Palladium (II) complexes against various Human Tumor cell lines, *Bioinorgchem Appl-v* 2008, PMC2615113 **(2008)**

14. Santhakumari R. and Ramamurthy K. Structural, Thermal and optical characterization of an organic NLO material–Benz aldehyde Thiosemicarbazone monohydrate single crystals, *Spectro chemica Acta part A,* **78,** 653-659 **(2011)**

15. Formation charectrisation and structural studies of novel thiosemicarbazone Palladium (II) complexes. Vila JM, Pereira Mat, Ortigueira JM, etal., *J. Chemicalsocity*, Dalton Transations, **(23)**, 4193-4201 **(1999)**

16. Sethuraman K., Ramesh babu K., Vijayan N., Gobalakrishnan R. and Ramasamy P., Synthesis, growth of organic nonlinear optical crystal; Semicarbazone of 2-amino -5-chloro –benzophenone (S2A5CB) and its characterization, *Crystal growth,* **(290)**, 539-543 **(2006)**

17. Janarthanam S. Rajan Y.C, Umarani P.R., Selvakumar S., Pandi S., Synthesis and characterization of Semicarbazone p-Hydroxy-3-Methoxy acetophenone (SPH3MA) Single crystal, *Physica. B-condenced matter,* **(406)** 135-138 **(2011)**

18. Anbusrinivasan P., Madhurambal G. and Mojumdar S.C., Thermal and spectral properties and induction period, Intrafacial energy and nucleation parameters of solution grown Anthracene, *J Therm Anal Calorim,* **108,** 939-46 **(2012)**

19. William Kemp, Organic spectroscopy-*Third edition-* **(1991)**

20. Balakrishnan T. and Ramamurthi K., Crystalgrowth, Structural, optical, mechanical and thermal properties of a new non linear optical single crystal L-Ornithine monohydrochloride, *Spectrochimica Acta part A,* **72,** 269-273 **(2009)**

21. Mojumdar S.C., Miklovic J., Krutosikova A., Valigura D. and Stewart J.M., Furopyridine-Ni(II) complexes-Synthesis, Thermal and spectral characterization, *J Therm Anal Calorim.,* **(81),** 211-215 **(2005)**

22. Narayanamoolaya B. and Dharmaprakash S.M., Synthesis, growth and characterization of nonlinear optical crystal L-tyrosine hydro bromide, *J Crystal growth*, **290,** 498-503 **(2006)**

23. Ramesh Babu R., Ramesh R. Gopalakrishnan R., Ramamurthi K., Bhagavannarayana G., Growth, Structural, optical, mechanical and optical properties of pure and metal ions doped sulphamic acid single crystals, *Spectrochimica Acta part A,* **76,** 470-475 **(2010)**

24. Mojumdar SC. Thermoanalytical and IR spectroscopy investigation of Mg(II) complexes with hetrocyclic ligands, *J Therm Anal Calorim*, **(64),** 629-36 **(2001)**

25. Madhurambal G., Mojumdar S.C., Hariharan S.and Ramasamy P., TG,DTC,FT-IR and Raman spectral analysis of ZN\Mg, Ammoniumsulphate mixed crystals; *J Therm Anal Calorim,* **(78)**, 125-33 **(2004)**

26. Preema. C Thomas, Langabhushankumar, A. Anuradha. S. Aruna, Ginsonp. Joseph, P. Sagayaraj, Growth and characterization of nonlinear optical single crystals of L-argininediiodate, *J.crystal growth,* **(290),** 560-564 **(2006)**

27. Sweta M. and Tamusree K., Growth and characterization of nonlinear optical crystal Zinc tris (thiourea) sulphate in presence of L-arginate, *Optical mat,* **30,** 508-512 **(2007)**

28. Jayalakshmi D. and Kumar J., Growth and characterization of bisthiourea Zinc acetate, *Cryst Res Technol ,* **41,** 37-40 **(2006)**

29. Porob R.A., Khan S.Z., Mojumdar S.C. and Verankar V.M.S., Synthesis, TG, SDC and infra-red spectral study of Nimn2(C2H4O4)36N2H4-A precursor for NiMn2O4 nanoparticles; *J Therm Anal Calorim,* **(86)**, 605-612 **(2006)**

30. Meera. K, Muralitharan R, Tripathi AK and Dhanasekaran R., Growth of Thiourea doped TGS crystals and their characterization, *J. Cryst Growth,* **260,** 414-421 **(2004)**

31. Mojumdar S.C., Thermoanalytical and IR spectroscopy investigation of Mg(II) complexes with hetrocyclic ligands, *J Therm Anal Calorim,* **(64),** 629-636 **(2001)**

32. Kurtz S.K. and Perry T.T, *J.Appl.Phys.,* **39,** 3798-3813 **(1968)**