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OPTICAL AND CONDUCTIVITY ANALYSIS OF THIOUREA SINGLE CRYSTALS

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ABSTRACT

The Thiourea single crystals have been grown from saturated solution by slow evaporation technique. The crystallinity and structure of pure thiourea single crystals were confirmed using powder XRD and frequency assignments of the various internal modes of vibrations for the functional groups were observed in the FTIR spectroscopy. Transparency and optical studies were carried out by UV-Vis spectroscopy. It shows a good transmittance in the entire visible region and the lower cut off wavelength at 241.67 nm attest the usefulness of this material for optoelectronics applications. Dielectric and conducting studies were done for analysis of its electrical properties. The low values of dielectric loss suggest that the grown crystals have lesser defects.

Keywords: NLO semi organic crystals, PXRD, FTIR, UV-VIS Studies, Electrical Studies

INTRODUCTION

Nonlinear optics plays an important role in the emerging era of photonics. Photonics involves the application of photons for information and image processing. Nonlinear optical processes have applications in vital functions such as frequency conversion and optical switching[1]. Organic crystals can have very large nonlinear susceptibilities relative to inorganic crystals, but exhibit low damage threshold and poor processibility.[2-5] In contrast, pure inorganic NLO materials typically have excellent mechanical and thermal properties, but often possess relatively modest optical nonlinearities due to their lack of extended electron delocalization. Inorganic crystals grown from high temperature melts may typically have lower laser damage thresholds, and more optical in homogeneities throughout the bulk, due to impurities and defects resulting from the extremely non-equilibrium growth conditions.[6-10] In order to retain the merits and overcome the shortcomings, some new classes of NLO crystals such as semi organic crystals have been developed. Semi organic crystal is one in which the typically high-optical nonlinearity of a purely organic ion is combined with the favorable mechanical property and thermal properties of an inorganic counter ion.[11-12]

Semi-organic materials possess large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness compared to organic and inorganic materials.[13-16] Hence, much attention has been paid to grow new semi-organic nonlinear optical materials, in view of their potential applications in the field of telecommunications, optical information storing devices and second harmonic generation.[17-19] The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network of hydrogen bonds.[20]

EXPERIMENTAL

The thiourea single crystals have been grown from saturated solution by slow evaporation technique. The saturated solution was prepared by taking 100 ml of distilled water in a beaker and finely powdered 18.75 grams of thiourea. The substance was added in pinches till it gets completely dissolved. For promoting the solubility, the solution was stirred well with the magnetic stirrer and the process was continued until the last pinch of the substance was dissolved. Then the solution was filtered using filter paper. The top of the beaker was covered with polythene paper and make few small holes. This beaker was kept at room temperature without any disturbance. The single crystals were harvested between 10 to 15 days. Photographs of pure thiourea single crystals are shown in Fig.-1.

Fig.-1: Grown pure thiourea single crystals

Characterization of Crystals

Pure thiourea crystals were subjected to powder X-ray diffraction studies. The X-ray powder diffraction pattern of the grown crystals was obtained using XRD-ULTIMA 111 diffractometer and diffraction peaks are indexed. Functional groups are identified by FT-IR studies on the grown crystals which is carried out using a FT-IR Perkin Elmer RX-1 spectrophotometer, over a range of 400-4000 cm^{-1} KBr using pellet method. The proposed assignments of the various internal modes of vibrations were observed in the spectra. Optical transmission and absorption spectral analysis have been measured using a UV-Perkin Elmer Lampda 35 spectrophotometer over a wavelength range of 200-1200 nm. The transmission is uniformly high (99%) for light in the visible region of the electromagnetic spectrum, which could be capitalized useful for device application[21]. Polished section of the samples with known dimensions was subjected to dielectric measurement using a Dielectric-LCRZ meter TH2816A with a conventional two terminal sample holder.

RESULTS AND DISCUSSION

XRD Analysis

Pure thiourea crystals were subjected to powder X-ray diffraction studies. The X-ray powder diffraction pattern of the grown crystals was obtained using XRD-ULTIMA 111 diffractometer. The scanning rate was maintained over a 2θ range of 10° to 80° employing the reflection mode for scanning. The crystallinity of pure thiourea single crystals was confirmed by this analysis and diffraction peaks are indexed. These are shown in Fig.-2 and intensity with corresponding d values are shown in Table 1. The well defined, sharp peaks in the XRD patterns signify the good crystalline and single phase nature of pure thiourea crystals[22].

FT-IR Analysis

FT-IR studies on the grown crystals were carried out using a FT-IR Perkin Elmer RX-1 spectrophotometer, over a range of 400-4000 cm^{-1} KBr using pellet method. Fig. 3. shows the FTIR spectra of pure thiourea crystals. The proposed assignments of the various internal modes of vibrations were observed in the spectra. Thiourea, which is potentially capable of forming coordinate bonds through both sulphur and nitrogen, has been explained using infrared spectra of the crystals. The absorption band in the frequencies 3366, 3261cm^{-1} are due to the asymmetric stretching modes of NH_2.

The NH_2 symmetric stretching was observed at 3158 cm^{-1}, and the band at 1586 cm^{-1} could be assigned to NH_2 bending. The CN and CS asymmetric stretching vibrations were observed at 1464 and 1428 cm^{-1}. The CN and CS symmetric stretching vibrations were observed at 1088 and 729 cm^{-1}. The absorption bands observed at 626 and 487 cm^{-1} could be correlated with the NCN asymmetric bending vibrations[23-25]. The modes of vibrations of the pure thiourea are summarized in the Table-2.

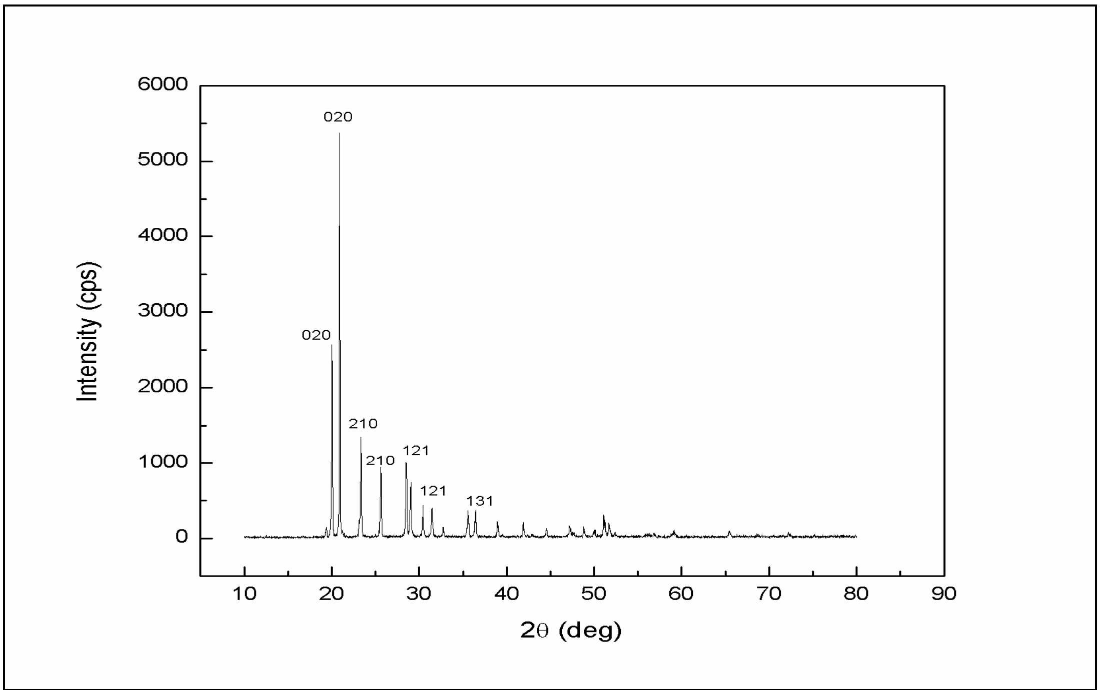

Fig.-2: Powder X-ray diffraction patterns of grown thiourea single crystals

Table-1: XRD data for Thiourea crystal

2θ (degree)	d-value	Intensity (cps)	$I/I_{0\,(\%)}$
19.380	4.5764	137	4
20.040	4.4271	2240	54
20.900	4.2468	4177	100
23.360	3.8049	1217	30
25.620	3.4741	903	22
28.520	3.1271	997	24
29.040	3.0723	743	18
30.440	2.9341	390	10
31.460	2.8413	400	10
35.580	2.5211	357	9
36.420	2.4649	330	8
38.940	2.3110	217	6
41.900	2.1543	153	4
51.080	1.7866	313	8

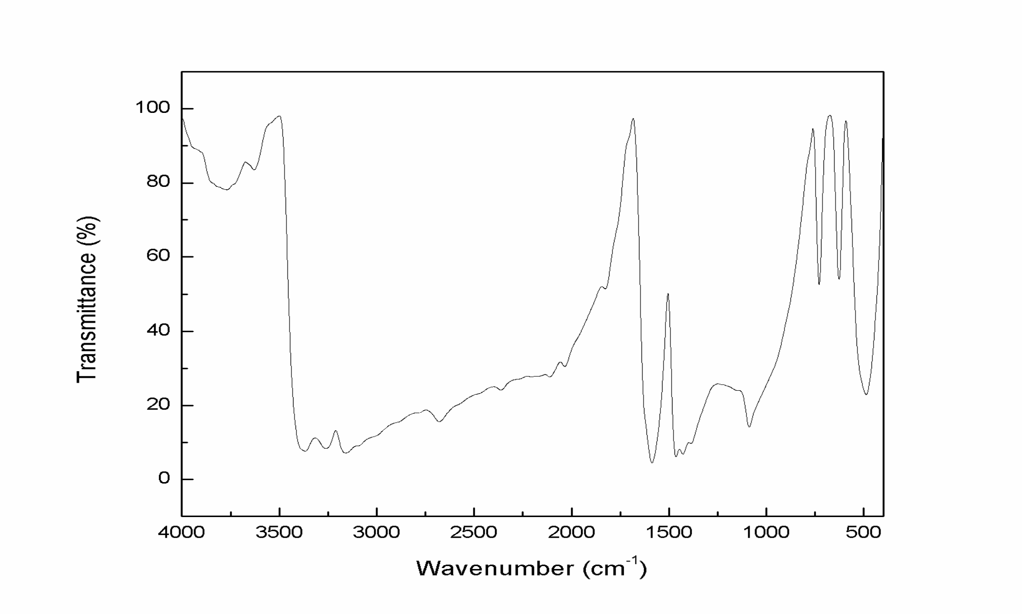

Fig.-3: FTIR spectra of grown thiourea single crystals

Table-2: Vibration modes observed in the Thiourea crystals

Pure Thiourea Wave number (cm^{-1})	Band Assignments
3366.89	NH_2 asymmetric stretching
3261.61	NH_2 asymmetric stretching
3158.94	NH_2 symmetric stretching
1586.76	NH_2 bending
1464.06	C-N asymmetric stretching
1428.37	C=S asymmetric stretching
1088.12	C-N symmetric stretching
729.08	C=S symmetric stretching
626.89	N-C-S asymmetric bending
487.25	N-C-N asymmetric bending

UV-Vis Analysis

The UV-Vis spectral analysis has been measured using a UV-Perkin Elmer Lampda 35 spectrophotometer over a wavelength range of 200-1200 nm. Generally, optical transmission spectrum gives valuable information about the structure of the molecule, as its absorption of UV and Visible light involves in the promotion of electron in σ and π orbital from the ground state to an higher energy state. From device point of view, the transmission spectrum is important, as the grown crystal can be used only in the highly transparent region. The recorded optical transmission spectrum was shown in fig.4. Here, the crystal shows a good transmittance in the entire visible region. The lower cut off wavelength at 241.67 nm combined with the above, attest the usefulness of this material for optoelectronics applications[26-27].

The absorption spectrum was recorded in the wavelength region from 200 to 1200 nm. The UV-Visible absorbance spectrum of thiourea crystal is shown in fig. 5. The absorption spectrum reveals that in thiourea crystal there is strong absorption in 190 to 300 nm.

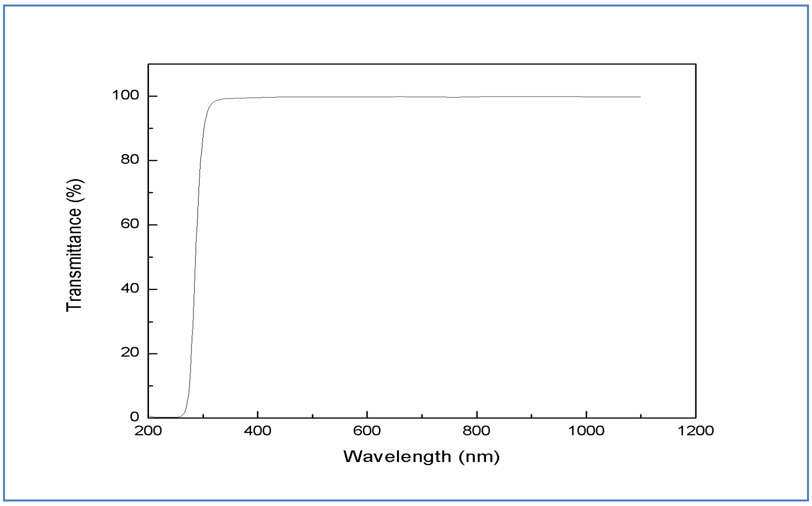

Fig.-4: Transmission spectra of grown thiourea single crystals

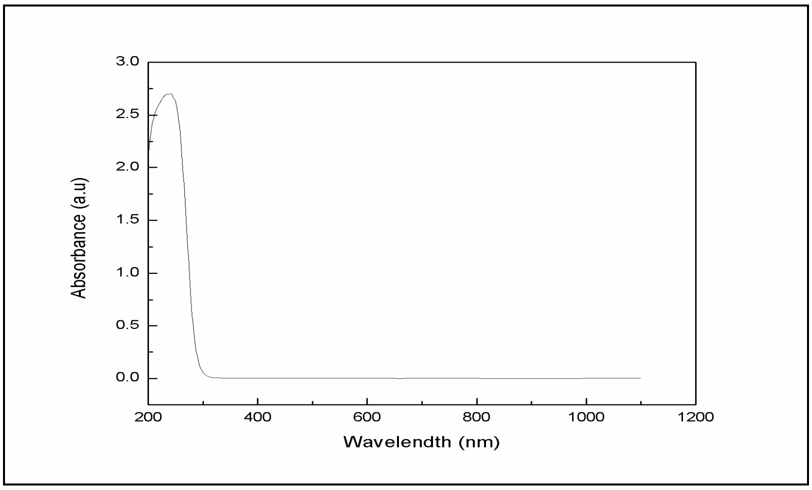

Fig.-5: Absorption spectra of grown thiourea single crystals

Electrical studies- Dielectric and conductivity Analysis

Polished section of the samples with known dimensions was subjected to dielectric measurement using a Dielectric-LCRZ meter TH2816A with a conventional two terminal sample holder. The samples of pure thiourea were placed between the two copper electrodes by forming a parallel plate capacitor. The capacitance on the sample was then measured by varying the frequency from 50 Hz to 200 KHz. Fig. 6. shows the variation of dielectric constant of pure thiourea as a function of frequency. Here, initially the dielectric constant of pure thiourea was found to have high values at low frequency and then decrease with increase in frequency. The dielectric constant could be derived using the formula-

$$\varepsilon_r = Cd / \varepsilon_0 A$$

Fig.-7 shows the dielectric loss of pure thiourea as a function of frequency.

The low values of dielectric loss suggest that the grown crystals have lesser defects. The nature of variation of dielectric constant and dielectric loss as a function of frequency is almost the same.

Fig.8 shows the resistivity of pure thiourea as function of frequency. This also has high values at low frequency. The resistivity was derived using the relation-

$$\rho_{AC} = A / 2\pi fcd \ (\Omega m)$$

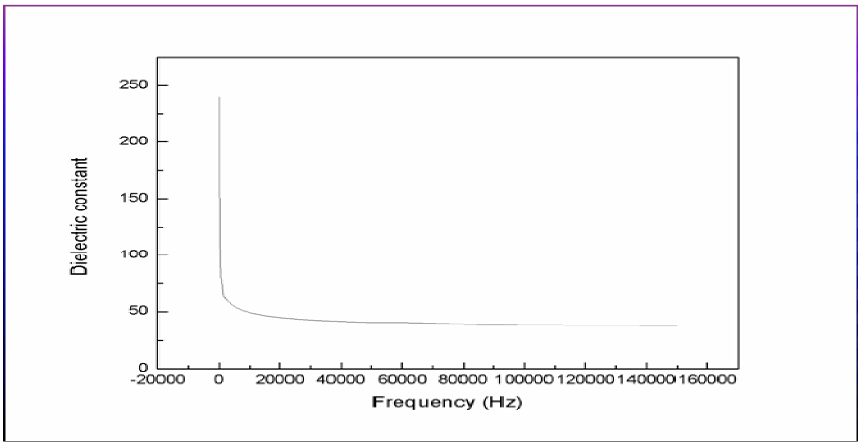

Fig.-6: Dielectric constant analysis for Thiourea

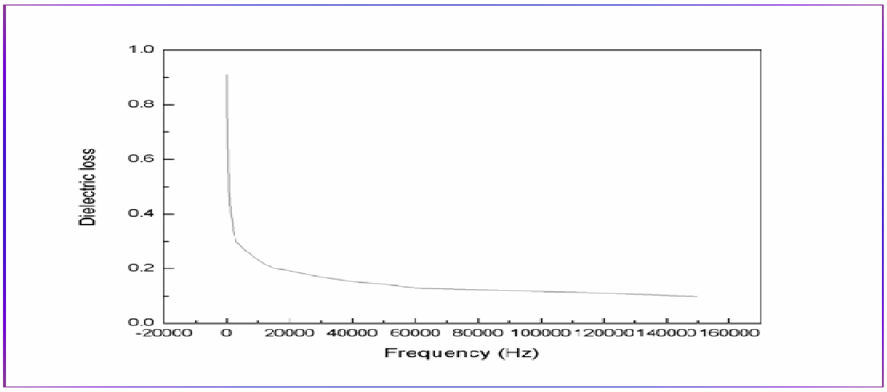

Fig.-7: Dielectric loss analysis for Thiourea

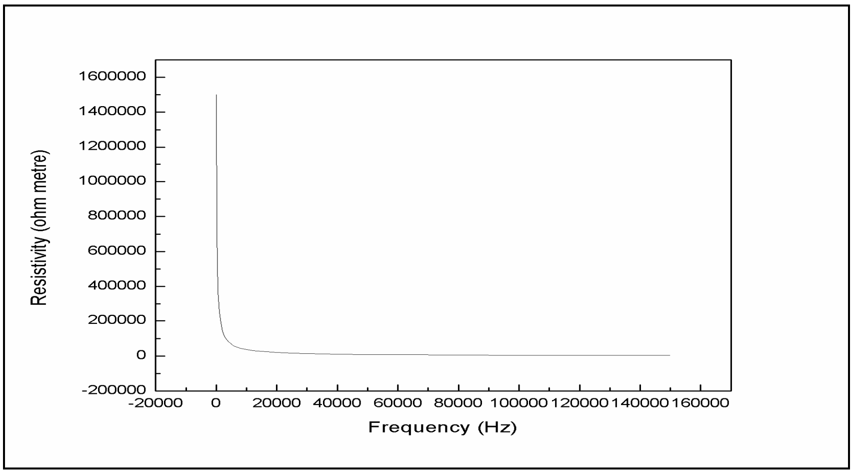

Fig.-8: Resistivity variations of Thiourea crystals with frequency

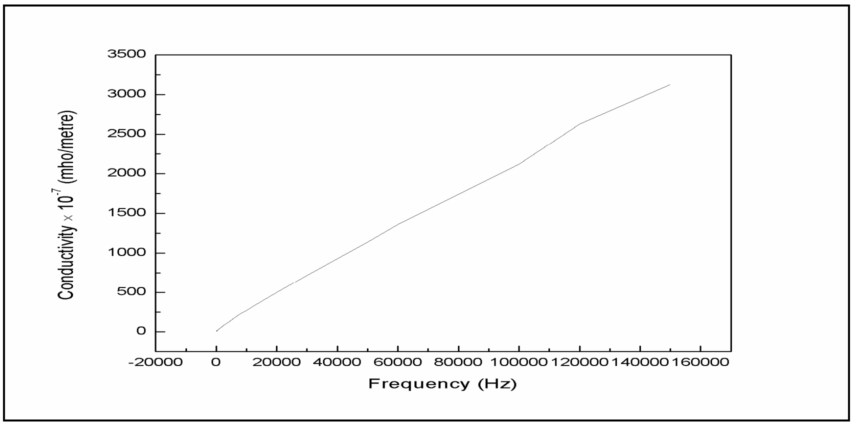

Fig.-9 Conductivity variations of Thiourea crystals with frequency

CONCLUSION

Highly good quality single crystals of thiourea were grown from saturated solution by slow evaporation method. FTIR spectrum confirmed the presence of functional groups and vibration modes were observed and assigned. The UV transmission, absorption spectrum reveal the thiourea crystal to possess a strong absorption in 190-300 nm region and good transmittance in the entire visible region. XRD analysis confirmed the formation of the material and their crystalline nature. The variations in dielectric constant, dielectric loss, conductivity and resistivity were studied under different frequencies, revealing a low dielectric loss.

REFERENCES

1. P. N. Prasad and D. J.Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, John-Wiley and Sons Inc, New York, (1991).
2. D.Ledoux, A.Lepers, J.Perigaud,J.Badan, and J.Zyss, *Opt.Commun.,* **80**, 149 (1990).
3. S.X.Dou, D.Josse, and J.Zyss, *J. Opt. Soc. Am. B*, **10**, 1708 (1993).
4. G.Knopfle,R. Schlesser, R. Ducret, and Gunter, *Nonlinear Opt.,* **9**, 143 (1995).
5. C.Serbutoviez, C.Bosshard, G. Knopfle, P.Wyss, P.Pretre, P.Gunter, K.Schenk, E.Solari, and G.Chapuis, *Chem. Mater.,* **7**, 1198 (1995).
6. N.R.Dhumane, S.S.Hussaini *et al.*, *Appl. Phy. A: Mat. Sci. and Proc*, **95**, 3 (2009).
7. G.Madhurambal, M.Mariappan, *Ind.J.Pure and Appl. Phy.*, **48**, .264 (2010).
8. C.Krishnan, P.Selvarajan, , *J. Expt. Sci*., **1**,3 (2010).
9. T.Thaila, S.Kumara Raman, *Archives Appl. Sci. Res,***3**, 1 (2011).
10. J.Thomas Joseph Prakash, M.Lawrence, *Inter. J. Comp. Appli*., **8**, 3 (2010).
11. K.Nagarajan, S.Kumara Raman, R.Sundaram, *Cry. Res. Tech*., **44**, 4 (2009).
12. Z.Kotler, R. Hierle, D.Josse, J. Zyss, and R.Masse, *J. Opt. Soc. Am. B*, **9**, 534 (1992).
13. S.Velsko, "Laser Program Annual Report", Lawrence Livermore National Laboratory, Livermore, CA, (1990).
14. N.B.Singh, T.Henningsen, R.H. Hopkins, R.D. Mazelsky, E.P.Hamacher, F. Supertzi, D.E.Hopkins, O. Zelmon, P.Singh, *J. Cryst. Growth.,* **128**, 976 (1993).
15. R.Mohan Kumar, D.Rajan Babu, D. Jayaraman, R.Jayavel, and K.Kitamura, *J. Cryst. Growth,* **275**, e1935 (2005).
16. J.Badan, R. Hierle, A. Perigand, J. Zyss, In and D.J. Williams,(Ed.). "Nonlinear Optical Properties of Organic Molecules and Polymeric Materials", 233 D.5, American Chemical Society, Washington, DC, (1993).
17. S.Kalainathan, R.Ezhil Vizhi, *Ferroelec*., **332,** 1 (2006).
18. Sweta Moitra, Tanusree Kar, *Mat. Chem and Phy*., **1**,17 (2009).
19. N.R.Dhumane, S.S.Hussaini, *Recent Res. in Sci. and Tech*., **2**, 10, (2010).

20. K.H. Landolt Bornstein Hellwege, A.M.Hellwage, "Numerical Data and Function Relationship in Science and Technology", Springer group, Berlin, (1982).
21. C.Krishnan, P.Selvarajan, T.H.Freeda, *Mat. and Manu Proc*., **23**, (2008).
22. D.Jayalakshmi, J.Kumar, *Cry. Res. Tech*., **41**, 1 (2006).
23. S.Selvakumar, K.Rajarajan, *Cry. Res. Tech*., **41**, 8 (2006).
24. M.Lydia caroline, S.Vasudevan, *Cur. Appl. Phy.,* **9** (2009).
25. S.Selvakumar, S.M.Ravikumar, *Mat. Chem and Phy*.,**103**, (2007).
26. S.Selvasekarapandian, K.Vivekanandan, *Cry. Res. Tech*., **32**, 2 (1997).
27. Fernando Loretta, T.Josephine Rani, *World J sci. and Tech*, **1**, 3 (2011).

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