Growth and Characterization of Pure and Anthranilic Acid Dopedbis Thiourea Zinc Chloride

Sr.A.Motcha Rakkini[1] Mrs.M.Jaya Brabha[2]
[1,2]Department of Chemistry
[1,2]Annai Velankanni College, Tholayavattam-629 174, Tamil Nadu, India

Abstract— Nonlinear optical of pure and Anthranilic acid doped Bis thiourea Zinc chloride were grown by slow evaporation technique. The grown crystals have been subjected to powder X-ray diffraction to determine the crystalline size and unit cell parameter. The incorporation of Anthranilic acid in BTZC was confirmed by FTIR analysis. UV-Visible spectrum shows that the grown crystals have wide optical transparency in the entire visible region. The thermo gravimetric analysis suggests that incorporation of Anthranilic acid in the BTZC increases the thermal stability of the grown crystal.

Key words: BTZC crystal, doping, EDAX, FTIR, UV, NLO material

I. INTRODUCTION

Semi organic nonlinear optical materials posses wide range of application in the field of telecommunication optical information storage devices. These materials have large nonlinearity, sensitivity and good mechanical hardness (1-3) recently metal complexes of thiourea have been explored. Some of the potential thiourea complexes are Bis thiourea zinc chloride(BTZC), Zinc thiourea sulphate(ZTS), Cadmium thiourea chloride(CTC), Bis thiourea Zinc acetate(BTZA) and Cadmium thiourea acetate(BTCA) (4-6). These crystals have better nonlinear optical property than KDP, higher laser damaged threshold, polarizibility and wide spectral transmission window, hence may be used for various NLO applications such as electro optic modulation, optical data storage and frequency conversion application.

The importance of amino acids in NLO application is in the fact that all amino acids contain an asymmetric carbon atom and crystallize in a non-centrosymmetric space group. In solid state, amino acids containing one de-protonated carboxyl group (COO-) and a protonated amino group ($NH3^+$). (7-10) many members of amino acids exhibit nonlinear optical properties. Some of the amino acids are used as dopants as they enhance the nonlinearity due to the presence of NH_2 and COOH groups. Growth of BTZC single crystals using slow evaporation technique at room temperature has already been reported. Anthranilic acid is the simplest of all amino acids in the crystalline form. In this work obtained Anthranilic acid doped BTZC crystal prepared by slow evaporation growth method. (11-15) the grown crystal was subjected to optical, structural and thermal characterization to study its possible use in optoelectronic and laser based application. The powder X-ray diffraction confirmed the orthorhombic structure.The incorporation of Anthranilic acid in BTZC crystal bonding was confirmed by FTIR spectra.(16-23) The UV –Visible absorption spectrum was obtained to observe the change in the optical absorption spectrum was obtained to observe the change in the optical absorption of BTZC crystal after addition of Anthranilic acid. The thermal study of grown crystal was carried out using the thermo gravimetric analysis (TGA).

II. MATERIALS AND METHODS

Anthranilic acid doped Bis thiourea zinc chloride crystals have been prepared by slow evaporation technique method.

The BTZC salt was synthesized by dissolving zinc chloride and thiourea in the ratio 1:2 in deionized water. Single crystals of BTZC and Anthranilic acid doped BTZC were grown employing slow evaporation techniques. The solution was stirred with magnetic stirrer at room temperature. The required quality of zinc chloride and thiourea was estimated from the following reaction.

$$Zncl_2 + 2[CS(NH_2)_2] \rightarrow Zn[CS(NH_2)_2]_2Cl_2$$

The calculated amount of salt was dissolved in the deionised water by constant stirring till super saturation stage was achieved. The purity of the synthesized salt was increased by successive recrystallization process. After 30 days a well defined transparent colorless BTZC crystal was harvested. For the growth of Anthranilic acid doped BTZC single crystals with good transparency were harvested in 30 days. The photograph of the grown crystals is shown in figure.

Fig. 1: The photograph of BTZC

Fig. 2: The photograph of Anthranilic acid doped BTZC

III. RESULT AND DISCUSSION

The structural and optical behavior of the grown crystals were examined by powder X-ray diffraction, and thermal properties EDAX, FTIR, and UV –Visible studies respectively.

A. Powder X-Ray Diffraction Analysis

The powder X-ray diffraction of grown Anthranilic acid doped BTZC crystal was carried out by using the powder X-

ray diffractometer employing CuKα radiation (λ=1.5406A^o). Using stimulated hkl values and experimental d values, The Bragg' reflection in the powder XRD patterns were indexed for pure and Anthranilic acid doped BTZC crystals. It was observed that the relative intensities have been changed and a slight shift in the peak position was observed as a result of doping. The most prominent peaks with maximum intensity of the XRD patterns of pure and doped specimens are quite different. The observations could be attributed to strain in the lattices. Appearance of sharp and strong peaks confirms the good Crystallinity of the grown sample. The prominent well resolved Bragg's peak at specific 2θ angle reveals the high perfection of the grown crystal the observed values are in good agreement with the reported values. When comparing the pure and Anthranilic acid in BTZC crystal powder XRD pattern there was variation in the doped XRD of BTZC crystals. This confirms the incorporation of Anthranilic acid in BTZC. The average crystalline size Anthranilic acid doped BTZC crystal is found to be 48.8181x10^{-9}m.

2Theta	**FWHM**	**Size**	**Plane**
13.854	0.172	48.6287	111
15.512	0.118	71.0232	200
27.611	0.166	51.4994	111

Table 1: XRD parameters of Bis thiourea Zinc chloride

2Theta	FWHM	Size	Plane
13.913	0.164	51.0096	111
15.603	0.172	48.7269	200
16.886	0.176	47.6887	002
20.645	0.173	48.7777	201
27.712	0.171	50.0056	111
30.670	0.184	46.7004	002

Table 2: XRD parameters of Anthranilic acid doped Bis thiourea Zinc chloride

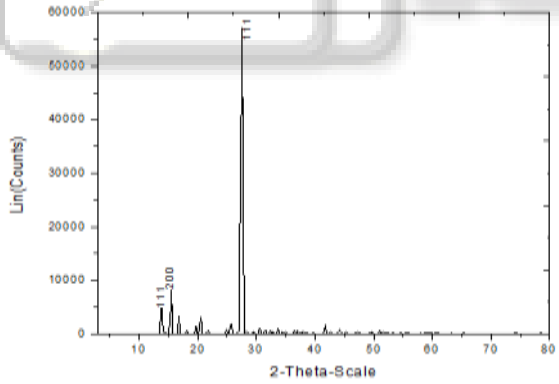

Fig. 3: XRD Pattern of Bis thiourea Zinc Chloride

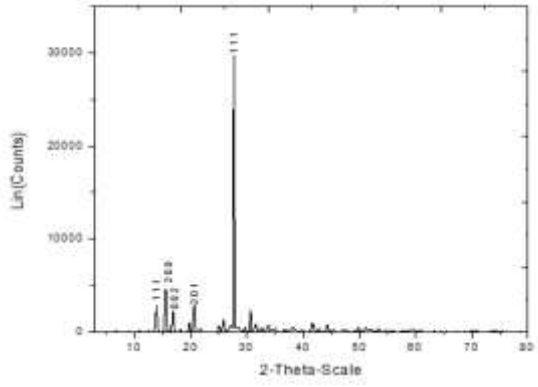

Fig. 4: XRD spectrum of Anthranilic acid doped BTZC

B. Fourier Transforms Infrared Spectroscopy (FTIR) Analysis

In order to analyze the presence of Anthranilic acid in BTZC crystal qualitatively, Fourier transform infrared spectra carried out. FTIR spectrum was recorded in the wavelength range 500-4500cm-^{1}. The FTIR spectra of pure and Anthranilic acid doped BTZC crystal was shown in figure), Fig.5, shows the intensity 3285.96cm^{-1} is due to Asymmetric NH_2 stretching vibration. The peak observed at 3200.55cm^{-1} is assigned to symmetric NH_2 stretching vibration. The Asymmetric C=S stretching vibrations occurs at 1404.25cm^{-1}. The peaks at 1614.21cm^{-1} is due to NH_2 bending vibration. In Anthranilic acid doped BTZC, the extra NH_2 group could not easily expressed in the spectrum. Because of its larger aryl (C_6H_4) ring. Symmetric N-C-N stretching vibration peak at 1099.76cm^{-1}. Asymmetric N-C-N stretching vibration peak at 1493.36 cm^{-1} the symmetric C=S stretching vibrations occurs at 712.57cm^{-1}. The Anthranilic acid doped BTZC absorption bands are compared to pure BTZC, there is slight variations occur. This shift may be due to doping of Anthranilic acid.

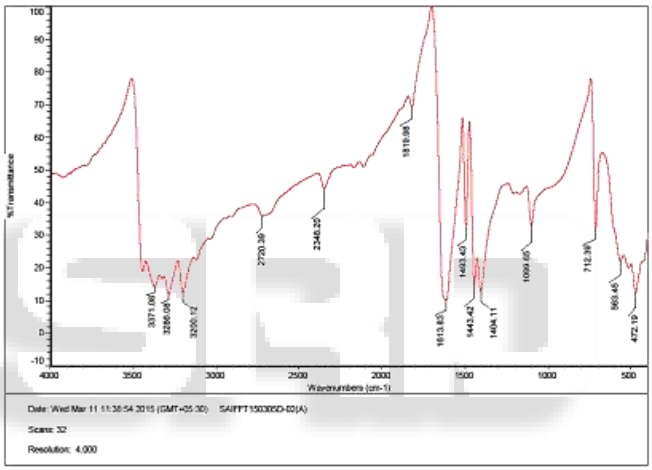

Fig. 5: FTIR Spectrum of Bis thiourea Zinc Chloride

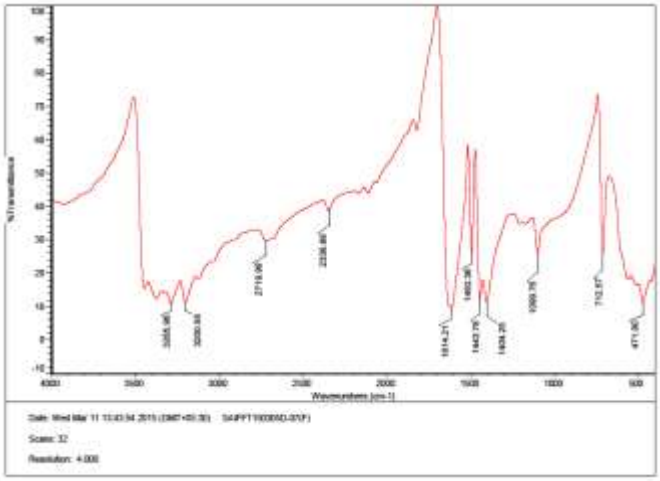

Fig. 6: FTIR Spectrum of Anthranilic acid doped Bis thiourea Zinc Chloride

Assignment	Thiourea (LR)	Pure BZTC	Anthranilic acid doped BTZC
AsymmetricNH_2 Stretching	3276.85	3286.08	3285.96
Asymmetric NH_2	3175.93	3200.12	3200.55

Stretching			
NH_2 Bending	1616.38	1613.83	1614.21
Asymmetric N-C-N Stretching	1468.32	1493.43	1493.36
Asymmetric C=S Stretching	1411.43	1404.11	1404.25
Symmetric N-C-N Stretching	1080.97	1099.65	1099.76
Symmetric C=S Stretching	727.83	712.39	712.57

Table 3: The Comparison and assignment of FTIR bands of pure and Anthranilic acid doped BTZC

C. UV-Visible Spectral Analysis

The single crystals are mainly used for optical application. Thus the study of optical transmission range of grown crystal was important. The optical transmission spectrum was recorded wavelength region 200-700nm.The transmittance spectra show the grown crystals have lower cutoff wavelength at around 232nm for BTZC crystal. The grown Anthranilic acid doped BTZC crystal has good transmission in UV as well as in visible regions. The forbidden band gap for the grown crystals of this work was calculated using the relation E=hc/λ, where 'h' is the plank's constant, 'c' is the velocity of light 'λ' is the cut-off wavelength. The grown crystal has good transmission in UV as well as in visible region. This is an added in the field of optoelectronic applications. The band gap and lower cut-off wavelength are shown in table.4. The lower cut of wavelength and low percentage of absorption indicates that the crystal readily allows the transmission of the laser beam in the range between the 300nm to 700nm. It shows that the grown crystal has a good transparency in UV, Visible and near IR region indicating that it can be used for NLO application(5). When compared to the pure and Anthranilic acid doped BTZC crystal, lower cut off wavelengthwais 0.29% is lower than the pure BTZC crystal. Which is likely to improve the optical property of BTZC. Anthranilic acid doped BTZC band gap energies are greater than pure BTZC. This high value of band gap shows the crystal posses dielectric behavior to induce polarization when powerful radiation is incident on the material. The large energy band gap also confirms that the defect concentration in the grown crystal was very low. The obtained value for the forbidden gap for pure and doped crystal shown in table.4.

Sample	Lower cut off Wavelength(nm)	Band gap energy(ev)
Pure BTZC	232	5.355
Anthranilic acid doped BTZC	231.71	5.36125

Table 4: Lower cut off wavelength and band gap energy of pure and Anthranilic acid doped BTZC

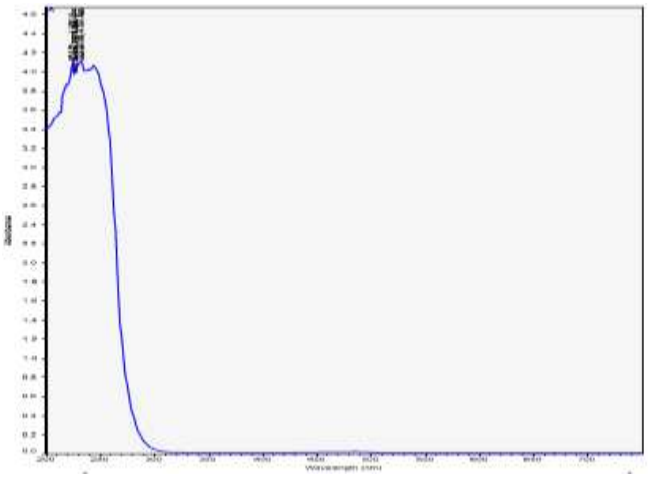

Fig. 7: UV Spectrum of Bis thiourea Zinc Chloride

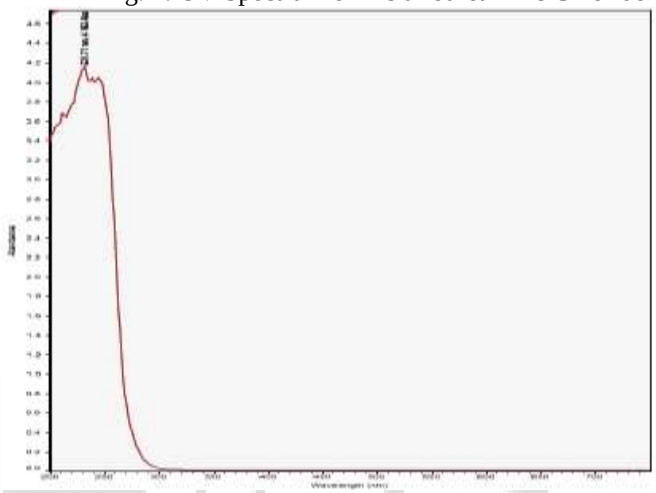

Fig. 8: UV Spectrum of Anthranilic acid doped BTZC

D. Thermal Analysis

Different Thermogram analysis(DTA) and thermo gravimetric analysis(TGA) gives information regarding the Phase transition temperature, melting point and the weight loss of the grown crystal, water of crystallization and different stages of decomposition of the pure and Anthranilic acid doped BTZC crystal system were determined by thermo gravimetric (TGA) by using TAQ-500 analyzer. Thermal analyzer in the temperature range 40^{o}C to 730^{o}C.

The TGA&DTA Spectrum of Anthranilic acid doped BTZC. The TGA curve shows that the sample undergoes a complete decomposition between 230^{o}C to 730^{o}C, this decomposition leads to a weight loss of about 25.65%, which may be due to the liberation of volatile substances like sulphur oxide and chlorine atoms and Anthranilic acid. Molecule and second weight loss occurs due to organic compound evaporation in 74.52%. There is no weight loss up to 243.10^{o}C, which indicates the melting point of the crystal and absence of water in the grown crystal. The thermal stability of Anthranilic acid doped BTZC crystal was higher than pure BTZC crystal. This temperature range of the grown crystals ensures the possibility of the crystals for NLO application.

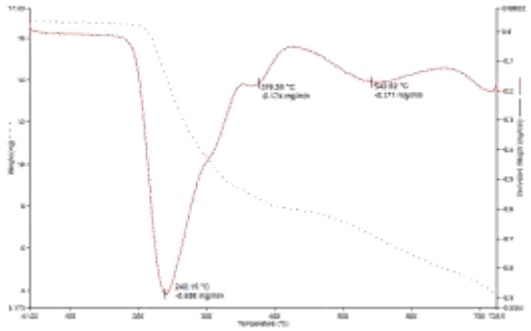

Fig. 9: TGA&DTA Spectrum of Bis thiourea Zinc Chloride

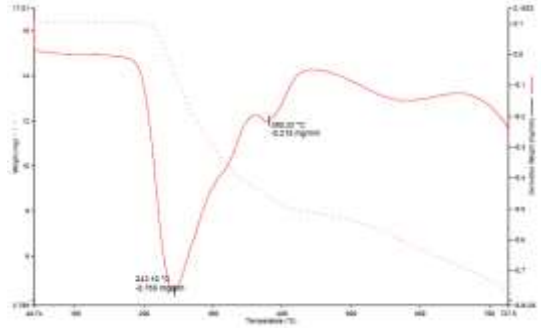

Fig. 10: TGA&DTA Spectrum of Anthranilic acid doped BTZC

E. EDAX Analysis

Energy dispersive X-ray analysis is important tool for determining the element present in the crystals. In the present investigation a small amount of material of the sample was subjected for EDAX analysis. EDAX spectrum of Anthranilic acid doped Bis thiourea Zinc Chloride is shown in Figure. The strong peaks observed in the spectrum are related to Nitrogen, Sulphur, Chloride, and Zinc. Anthranilic acid doped BTZC were found to have atomic percentage at 24.72of N, 29.99 of S, 29.92 of Cl, 15.37of Zn. Amino acids of Anthranilic acid doped BTZC does not present in the EDAX spectrum because there is no metal ions. In Anthranilic acid (C_6H_4 NH_2COOH) doped BTZC, the extra nitrogen atom could not easily expressed in the spectrum. Because of its larger aryl (C_6H_4) ring.

Crystal	Element	Weight %	Atomic %
Pure BTZC	N	26.21	50.27
	S	23.87	20.00
	Cl	26.54	20.11
	Zn	23.38	9.61
Anthranilic acid doped BTZC	N	10.26	24.72
	S	28.51	29.99
	Cl	31.45	29.92
	Zn	29.78	15.37

Table 5: EDAX data of the pure and Anthranilic acid doped BTZC crystal

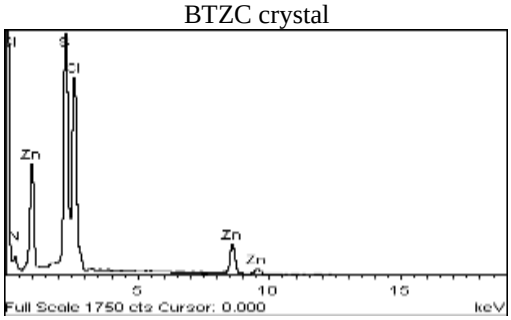

Fig. 11: EDAX Spectrum of Bis thiourea Zinc Chloride

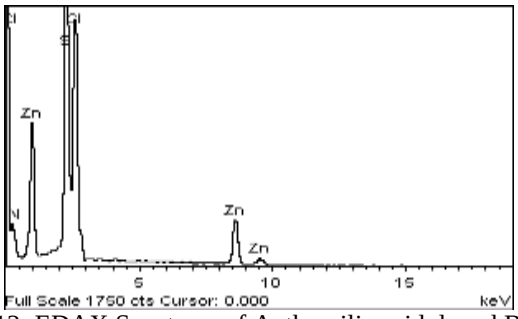

Fig. 12: EDAX Spectrum of Anthranilic acid doped BTZC

IV. CONCLUSION

Single crystals of pure and Anthranilic acid doped BTZC crystals were grown by the slow evaporation technique. Sharp peaks of powder XRD spectrum of the crystal was shown that the good crystalline nature of the compound. The presence of various functional groups was confirmed by FTIR analysis. UV-Visible study was shown that the grown crystal has wide range of transparency in UV and entire visible region and cutoff wavelength of Anthranilic acid doped BTZC was around 231.71nm. The lower cut off range of doped crystal got a good transparency than the pure crystal. The increase in thermal stability due to the presence of Anthranilic acid doped BTZC is observed from thermo gravimetric analysis. EDAX spectrum of Anthranilic acid (C_6H_4 NH_2COOH) doped BTZC, there are no metal ions and the extra nitrogen atom could not easily expressed in the spectrum. Because of its larger aryl (C_6H_4) ring. The promising crystal growth characteristics and properties of pure and Anthranilic acid doped BTZC crystal makes it suitable for optical devices applications.

REFERENCES

[1] J.Felicita vimala, J.Thomas Joseph Prakash, J.Felicita Vimala et.al/Elixir crystal growth, Volume 56 13355-13358 2013.
[2] V.Revathi, and V. Rajendran, Recent Research in science and Technology 4(2) 38-41, 2015.
[3] S. Chenthamarai, D. Jayaraman, C. Subramanian and P. Ramasamy, Materials Letters, Vol. 47, No. 4-5, pp. 247-251, 2001.
[4] K. Ambujam, K. Rajarajan, S. Selvakumar, A. Joseph and P. Sagayaraj, Journal of Crystal Growth, Vol. 286, No. 2, pp. 440-444, 2006.
[5] S. S. Hussaini, N. R. Dhumane, G. Rabbani, P. Karmuse, V. G. Dongre and M. D. Shirsat, Crystal Research and Technology, Vol. 42, No. 11, pp. 1110-1116, 2007.
[6] S. S. Hussaini, N. R. Dhumane, V. G. Dongre, P. Karmuse, P. Ghughare and M. D. Shirsat, Optoelectronics and Advanced Materials-Rapid Communications, Vol. 2, pp. 108-112, 2008.
[7] Kannan, N. P. Rajesh, R. Bairava Ganesh and P. Ramasamy, Journal of Crystal Growth, Vol. 269, No. 2-4, pp. 565- 569, 2004.
[8] K. Meera, R. Muralidharan, R. Dhanasekaran, P. Manyum and P. Ramasamy, Journal of Crystal Growth, Vol. 263, No. 1-4, pp. 510-516, 2004.
[9] M.-H. Jiang and Q. Fang, Advanced Materials, Vol. 11, No. 13, pp. 1147-1151, 1999.

[10] J. Ramajothi, S. Dhanushkodi and K. Nagarajan, Crystal Research and Technology, Vol. 39, No. 5, pp. 414-420, 2004.
[11] S. Ariponnammal, S. Radhika, R. Selva and N.Victor Jeya, Crystal Research and Technology, Vol. 40, No. 8, pp. 786-788 , 2005.
[12] M. J. Rosker, P. Cunningham, M. D. Ewbank, H. O.Marcy, F.R. Vachss, L. F. Warren, R. Gappinger and R. Borwick, Pure and Applied Optics, Vol. 5, No. 5, p. 667, 1996.
[13] K. Selvaraju, R. Valluvan, K. Kirubavathi and S. Kumararaman, Optics Communications, Vol. 269, No. 1, pp. 230- 234, 2007.
[14] S. Selvakumar, S. M. Ravikumar, K. Rajarajan,A. Joseph Arul Pragasam, S. A. Rajasekaran, K. Thamizharasan, P. Sagayaraj, Cryst. Growth and Design**.** 6, 2607,2006.
[15] S. Ariponnammal, S. Radhika, R. Selva, N. Victor Jeya, Cryst Res. Technol. 40**,** 786, 2005.
[16] S. Ariponnammal, R. Selva Vennila, S. Radhika, S. Arumugam, Cryst. Res. Technol. 40**,** 896, 2005.
[17] P. M. Ushasree, R. Jayavel, C. Subramanian,P. Ramasamy, J. Cryst. Growth. 197**,** 216,1999.
[18] R.Rajasekaran,K.V.Rajendiran,R. MohanKumar, . Jayaval, R. Dhanasekaran, P. Ramasamy, J. Mat. Chem and Phy 82, 273, 2003.
[19] R. Rajasekaran, P. M. Ushasree, R. Jayavel,P. Ramasamy, J. Cryst. Growth. 229, 563,2001.
[20] P. M. Ushasree, R. Muralidharan, R. Jayavel,P. Ramasamy, J. Cryst. Growth. 218, 365,2000.
[21] P. A. Angeli Mary, S. Dhanuskodi, Cryst. Res.Technol. 36, 1231, 2001.
[22] N. P. Rajesh, V. Kannan, M. Ashok, K. Sivaji,P. Santharaghavan, P. Ramasamy, J. Cryst. Growth. 262, 561, 2004.
[23] K. V. Rajendran, D. Jayaraman, R. Jayavel,P. Ramasamy, J. Cryst. Growth. 254, 461,2003.

