Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(12):359-365

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Thermal, surface and dielectric studies of L-glycyl alanine single crystals

P. Malliga

Department of Physics, Sathyabama University, Jeppiaar Nagar, Chennai

---

ABSTRACT

Single crystals of pure and thiourea doped Glycyl L-Alanine(GLA) were grown by slow evaporation method. The cell parameters were determined using single crystal X-ray diffraction method. To improve the physical properties of the GLA crystal, thiourea dopant was added by 2 mol%. EDAX studies confirm the presence of thiourea in the grown GLA crystal.The thermo gravimetric analysis (TG) and differential thermal analysis(DTA) of GLA and thiourea doped GLA(TU-GLA) crystals were performed by using TG / DTA Instrument. Dielectric constant measurements were carried out at different temperatures and frequencies. HR-SEM analysis was carried out in order to study the nature and surface features of the grown crystals.

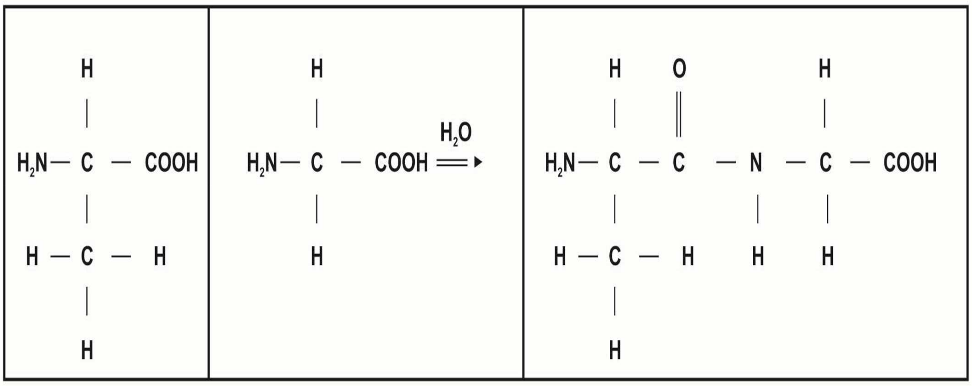
Keywords: Solution growth, XRD, EDAX, TGA, DTA, HR-SEM, Dielectric study.

INTRODUCTION

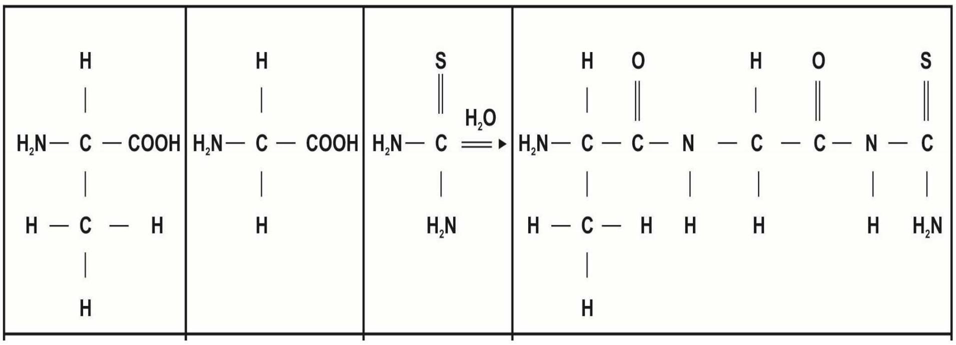
Recently, the growing of single crystals has helped advance modern technology. Nonlinear optical (NLO) materials have been studied extensively for their possible applications and are expected to play a major role in photonic technology such as telecommunication, optical computing, optical data storage and optical information processing [1-3]. A series of studies on semi-organic amino acid compounds such as L- argininium dinitrate [4], L- arginine hydrochloride[5], L- alanine acetate[6], and Glycine sodium nitrate[7] as potential NLO crystals have been reported. L- alanine is an amino acid, and it forms a number of complexes when reacted with inorganic acid and salts to produce an outstanding material for NLO applications. It is very clear from the previous reports that the physical properties of NLO crystals can be enhanced by doping with organic additives [8]. In this paper we report the study of the effect of thiourea on various physical properties of L-alanine single crystals. The present work gives a systematic study on the growth of pure Glycyl-L-Alanine (GLA) and thiourea doped GLA (TU-GLA) by low temperature solution growth method. An attempt has been made to improve the physiochemical properties of GLA by adding thiourea as dopant.

SYNTHESIS

The recrystallized salts of Glycine and L-Alanine (AR grade chemicals from E- Merck India Ltd) were used in the present crystal growth experiment. The GLA seed crystals were prepared by dissolving equimolar ratio Glycine and L-Alanine in Millipore water. The synthesized material was further purified by repeated recrystallization and it was used for the growth of GLA crystals. [Yield: 60%; Anal. (%) for $C_5H_{10}N_2O_3$: Found: C, 39.83%; H, 0.59%; N, 18.58%; Calc.: C, 41%; H, 0.6%; N, 19.17%. FT-IR (KBr disc, cm^{-1})1620 cm^{-1}($\nu_{CO=NH}$)]. The reaction that took place in L-Alanine and Glycine in water medium is as follows:



Similarly 0.2 M of thiourea salts was used for the growth of TU-GLA crystals respectively [Yield: 60% Anal. (%) for $C_6H_{12}N_4O_3$: Found: C, 34.16%; H, 4.61%; N, 26.32%; Calc.: C, 35.29%; H, 5.88%; N, 27.45%. FT-IR (KBr disc, cm^{-1})1620 cm^{-1}($\nu_{CO=NH}$); 820 cm^{-1}($\nu_{C=S}$)] single crystals. The structural formulae for thiourea doped GLA crystals is as shown below:



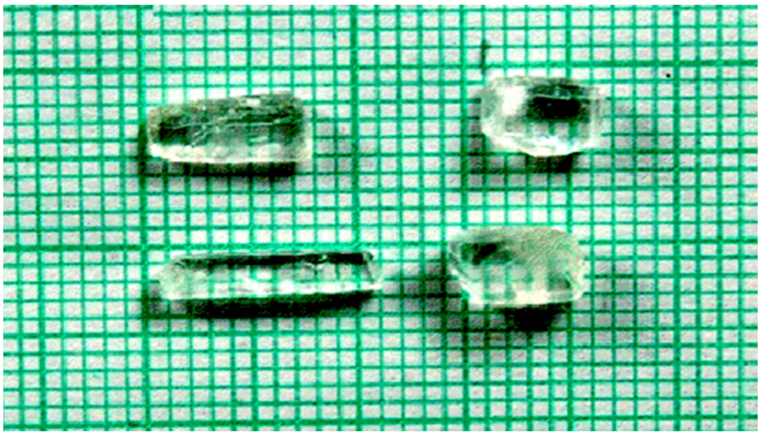


Figure 1 Photograph of grown crystal of GLA

GROWTH

The GLA solution was prepared in Millipore water and the temperature of the growth solution was maintained at 36°C using a constant temperature controller. Transparent good quality seed crystals formed due to spontaneous nucleation were used for growth experiments. Transparent single crystal of dimension10x8x4 mm^3 was obtained in a period of 30 days. The photograph of as grown crystals of Glycyl L-Alanine crystals is shown in Figure 1. Similarly crystals are also grown with thiourea as dopant. Saturated solution of GLA was prepared at room temperature and the solution was filtered and thiourea was doped in 2 wt% after adding the dopant the solution is again stirred well in a closed vessel for more than an hour and then the solution was filtered and dried in dust free atmosphere at 35˚C.

These crystals obtained with thiourea as dopant had no observable morphological changes. The as grown crystal of dimension 10x5x4 mm^3 is shown in Figure 2.

Figure 2 Photograph of grown crystal of TU-GLA

CHARACTERIZATION

SINGLE CRYSTAL XRD ANALYSIS

Single crystal X-ray diffraction (XRD) analysis of Glycyl L-Alanine was carried out using BRUKER axs kappa apex2 CCD diffractometer with MoKα (λ=0.71073Å) radiation. It is observed that Glycyl L-Alanine crystals crystallize in the orthorhombic system and belong to $P2_12_12_1$ space group which is recognized as non Centro symmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals. The lattice parameter values were calculated as a = 9.690 Å, b = 9.565 Å, c = 7.436Å. The volume of unit cell V=690 Å and compared with the literature values [9] and [10].

In the case of thiourea doped GLA crystals slight variations in lattice parameters as well as cell volume values are observed. The lattice parameter values were calculated as a = 9.695 Å, b = 9.564 Å, c = 7.437Å, with cell volume V=710 Å. The crystallographic data of GLA, TU-GLA and U-GLA crystals are shown in Table 1.

Table 1 Crystal data of GLA and TU-GLA

Crystal System	a Å	b Å	c Å	α	β	γ	Volume Å^3
GLA	9.690	9.565	7.436	90^o	96^o	90^o	690
TU-GLA	9.695	9.564	7.437	90^o	96^o	90^o	710

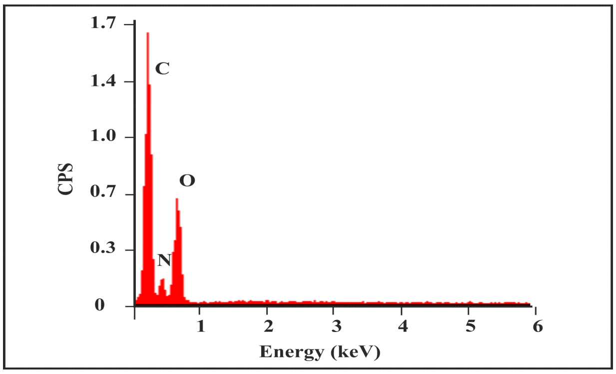


Figure 3 EDAX Spectrum of GLA

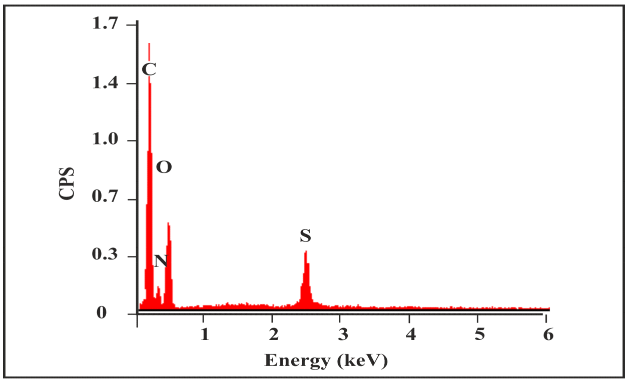


Figure 4 EDAX Spectrum of TU-GLA

ENERGY DISPERSIVE X-RAY ANALYSIS

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals. It is a microanalytical technique that uses the characteristic spectrum of X-rays emitted by the sample after excitation by high- energy electrons. The results obtained in the elemental analysis of GLA and TU-GLA crystals are shown in Figures 3 and 4. The EDAX spectrum confirms the presence of carbon, nitrogen, oxygen in GLA grown crystals. In TU-GLA crystals, the presence of sulphur confirms the inclusion of thiourea in the lattice of pure Glycyl L-Alanine crystals.

THERMAL ANALYSIS

The thermal behavior of GLA single crystal was studied in the temperature range from 100°C to 800°C using NETZSCH STA 409C/CD system. Figure 5 shows the TGA/DTA curves. The DTA curve indicates that the material has an exothermic peak at 241°C which represents the melting point respectively. The TGA curve of GLA indicates that the sample is stable from ambient up to 242°C with a weight loss of 33.62%. A systematic weight loss was observed as the temperature further increases above the melting point. The total weight loss of the sample is 98.4% at 300°C. It is observed that there is no phase transition or decomposition up to the melting point (235 °C) and also there is no mass reduction or decomposition up to 200 °C indicating that one can crystallize this material by slow solvent evaporation solution growth technique.

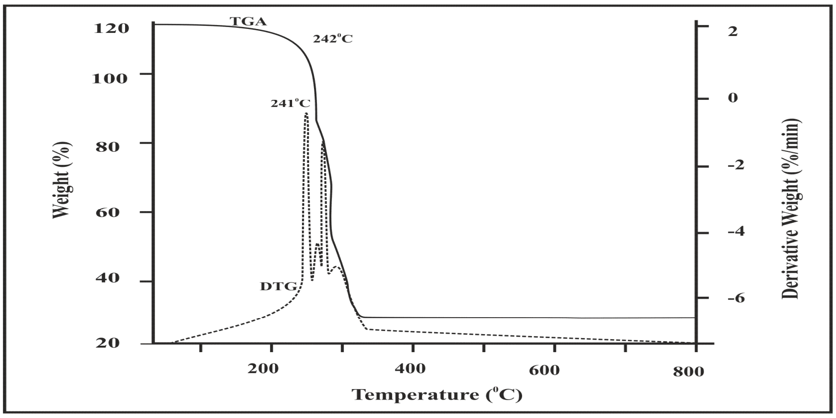


Figure 5 TG-DTA traces of GLA

The thermal stability of pure and doped GLA single crystal was estimated by TGA and DTA techniques. The TGA curve of TU-GLA indicates that the sample is stable from ambient up to 242°C with a weight loss of 33.62%. A systematic weight loss was observed as the temperature further increases above the melting point. The total weight loss of the sample is 98.4% at 300 °C. The DTA curve indicates that the material has an exothermic peak at 241 °C which represents the melting point respectively. It is observed that there is no phase transition or decomposition up to the melting point (241°C) and also there is no mass reduction or decomposition up to 200°C indicating that one can crystallize this material by slow evaporation solution growth technique. However in TU-GLA, the DTA peak is largely shifted to 245 °C .This increment in the decomposition temperature is evident for the doped crystals, suggesting that the substitution of thiourea enhances the thermal stability of GLA crystal. The TG-DTG traces of TU-GLA are shown in Figure 6.

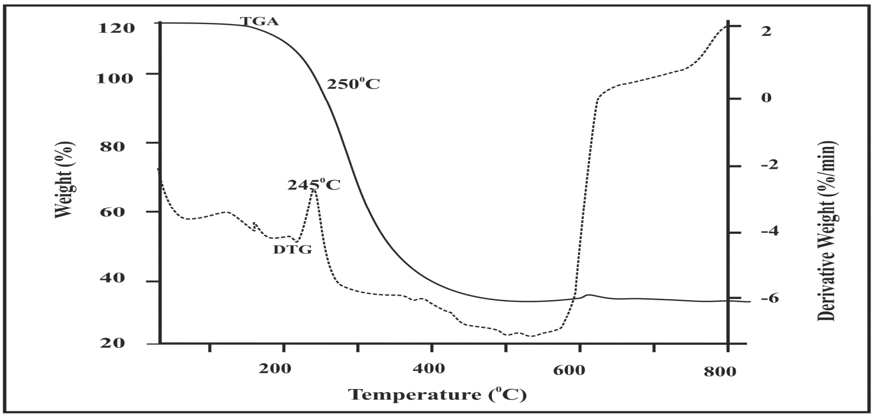


Figure 6 TG-DTA traces of TU- GLA

DIELECTRIC STUDIES

The dielectric analysis is an essential characteristic that can be used to get information based on the electrical properties of a material medium as a function of temperature and frequency. Based on this study, the ability of storing electric charges by the material and ability of transferring the electric charge can be evaluated.Dielectric properties are associated with electro optic property of the crystals; particularly when they are insulating materials[11,12].Electronic and Microelectronics industries need low dielectric constant materials as an interlayer dielectric [13].

The dielectric constant of GLA and TU-GLA crystals were studied at different temperatures using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. Figures 7 and 8 shows the plot of dielectric constant (ε_r) vs log frequency.

The dielectric constant has high values in the lesser frequency region and then drops with the applied frequency. The very high value of ε_r at low frequencies may be due to the existence of all the four polarizations namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations progressively. From the plot, it is also observed that dielectric constant decreases with increasing temperature, which depends on the purity and perfection of the sample. The variations of dielectric loss (tan δ) with frequency are shown in Figure 9 and 10. It is observed that the dielectric loss decreases with increasing frequency. The low value of dielectric loss indicates that the grown crystals are of moderately good quality. The larger values of dielectric loss (tan δ) at lower frequencies may be attributed to space charge polarization owing to charged lattice defects. It can be noted that the dielectric constant for TU-LAH are more than that of LAH at all frequencies region. The very low value of dielectric constant at higher frequencies is important for extending the material applications towards photonic, electro-optic and NLO devices.

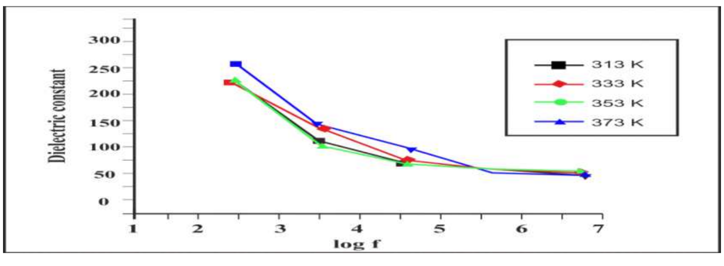


Figure 7 Variation of dielectric constant with log frequency for GLA

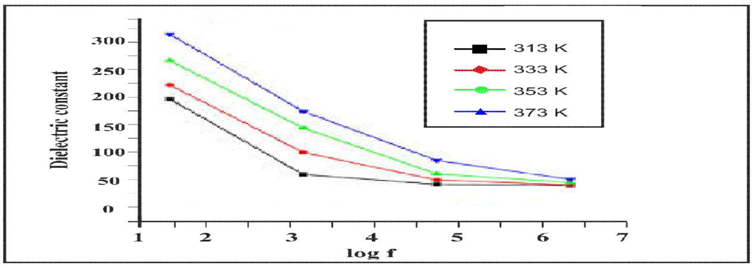


Figure 8 Variation of dielectric constant not with log frequency for TU-GLA

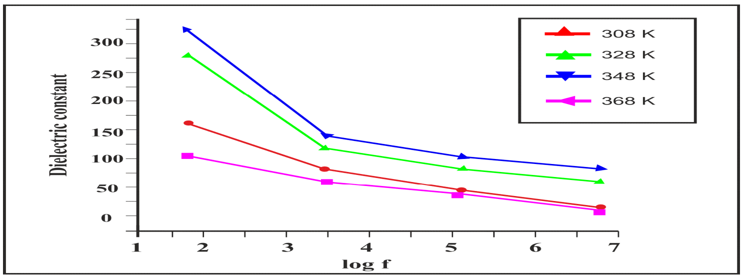


Figure 9 Variation of dielectric loss with log frequency for GLA

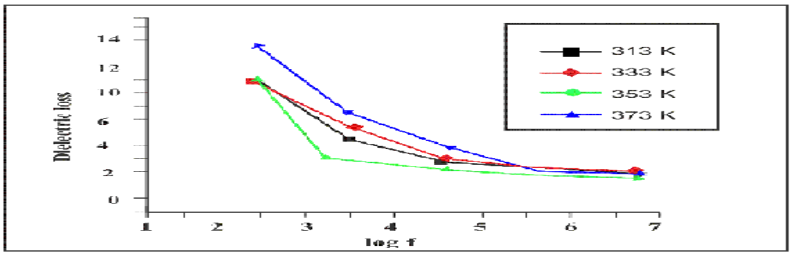


Figure 10 Variation of dielectric loss with log frequency for GLA

HR-SEM ANALYSIS

The micro-morphology of the growth axis was observed by a scanning electron microscopy (SEM) using JSM-253 SEM analyzer.The crystals were cut into few mm for observing the surface morphology. The SEM images of GLA and TU-GLA is shown in Fig.11 and 12. The HR-SEM micrograph reveals thatthe presence of dopant on the surface of the doped thiourea crystals. The HR-SEM studies reveal that the crystals are free from dislocations and impurities.

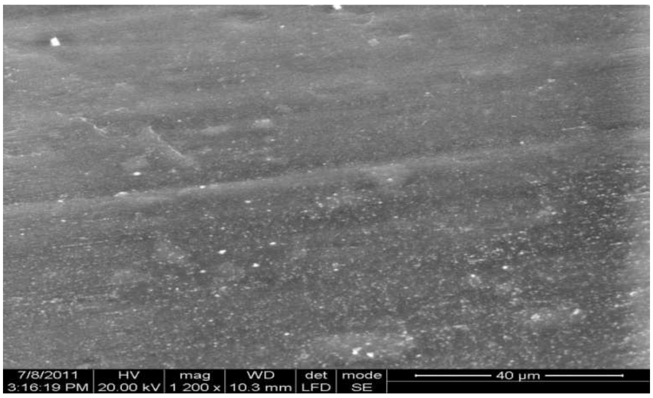


Figure 11 HR-SEM of GLA

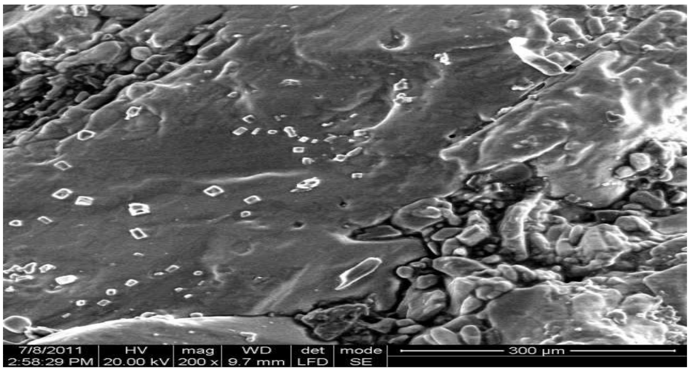


Figure 12 HR-SEM of TU-GLA

CONCLUSION

Single crystals of Glycyl L-Alanine (GLA) and thiourea GLA (TU-GLA) has been successfully grown by slow evaporation solution growth method at room temperature. The effect of thiourea dopant on crystal properties has been studied. Single crystal XRD analysis confirms the structure and change in lattice parameter values for the doped crystals. GLA and TU-GLA single crystals crystallize in the orthorhombic system and belong to $P2_12_12_1$ space group which is recognized as non centrosymmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals. The chemical composition and presence of sulphur in TU-GLA crystals was confirmed by EDAX analysis.

The TG/DTA analyses reveal that GLA is thermally stable up to 242 °C while TU-GLA upto 250 °C. Hence the crystals can be used as a potential material for photonic applications below this temperature.

Dielectric studies prove the low values of dielectric constant and dielectric loss in the samples at high frequency. The low value of dielectric constant and dielectric loss at high frequencies enhance the utility of the crystals in their applications. All the above studies confirm the suitability of the grown GLA and TU-GLA crystals for optical devices and optoelectronic devices.

REFERENCES

[1] N Vijayan; S Rajasekaran; G Bhagavannarayana; R Ramesh Babu; R Gopalakrishnan; M Palanichamy; P Ramasamy. *Cryst. Growth Des*., **2006**, 6 (11), 2441-2445.
[2] C Alosious Gonsago; Helen Merina Albert; P Malliga; A Joseph Arul Pragasam. *J Therm Anal Calorim***, 2011**, DOI 10.1007/s10973-011-1719-y.
[3] S Moitra; T Kar. *Cryst. Res. Technol*. **2010**, 45,70-74.
[4] C Preema. Thomas; Jolly Thomas; J Pakiam Julius; J Madhavan; S Selvakumar; P Sagayaraj. *J. Cryst. Growth.* **2005,** 277, 303-307.
[5] K Meera; R Muralidharan; E Dhanasekaran; M Prapun; P Ramasamy. *J. Cryst. Growth*.**2004**, 263,510-516.
[6] R Mohankumar; D Rajanbabu; D Jayaraman; R Jayavel; K Kitamura. *J. Cryst. Growth*. **2005**, 275, e1935-e1939.
[7] M Narayan Bhat; S Dharmaprakash. *J. Cryst. Growth*, **2002**, 236, 376-380.
[8] V Krishnakumar; S Sivakumar; R Nagalakshmi; S Bhuvaneswari; M Rajaboopathy. *Spectrochim. Acta.* **2008**, Part A71, 480-485.
[9] P R Tulip; S P Bates. *Molecular Physics***. 2008**,1-15
[10] P M Petrosoyan; R P Sukiyasan; H A Karpetyan; S S Tenzyan; R S Feigelson. *J. Cryst. Growth*, 213, **2003**, 103-111.
[11] S Boomadevi; H P Mittal. *J. of Cryst. Growth*, **2004**; 261:55-62.
[12] A Bose. etal. *Indian J. of Physics*.**2013**; 87: 977-981.
[13] C Balarew; R J Duhlew. *Solid state Chem***, 1984**; 55:1-6.