Growth and Characterization of Cu ions doped L-Threonine Single Crystals

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Abstract: - The Pure and Cu doped L-Threonine single crystals were grown from aqueous solution by slow evaporation technique. The density of the crystals was determined by floatation technique. The Unit cell parameters were determined from SXRD. Orientations of hkl planes were determined from Powder XRD data. The Presence of functional groups was qualitatively estimated by FT Raman spectrum. The dopant concentration of the crystals was estimated from EDX spectrum data. The Atomic Force Microscopy was taken to analyze surface morphology. The dielectric studies for all the crystals were carried out at different frequencies for various temperatures. UV-Vis-NIR spectrum was recorded to study the optical properties. The SHG efficiencies of the Cu doped crystals were found to be greater than that of KDP crystal.

Keywords: L-Threonine, Crystal growth, Unit cell Parameters, SXRD, FT Raman, Atomic Force Microscopy, Di electric, UV-Vis-NIR

1. INTRODUCTION

In view of potential applications in photonics and electronics industries, optical modulation, optical switching, optical rectification, optical communication, device fabrication etc., the Non linear materials (NLO) have been a great deal of attention in research for the past two decades [1-3]. The applications of NLO materials depend upon the knowledge of material properties such as optical transparency, birefringence, thermal, electrical properties and micro hardness. The organic material L-Threonine is a small naturally occurring polar and chiral amino acid. Generally, Organic materials exhibit large optical susceptibilities, inherent ultrafast response times and very high Second Harmonic Generation efficiency than that of inorganic materials but they have very poor thermal and mechanical strength [4-5]. In order to enhance the mechanical hardness of the crystals, Armington et al [6] suggested two methods i) solid solution hardening ii) impurity hardening. Several studies on L-Threonine single crystal have been reported [7-13]. In the present study, with intent to strengthen the organic material, the method of impurity hardening is attempted by doping the L-Threonine with the copper sulphate, an inorganic compound. Mechanical properties of the Cu doped L-Threonine crystals were already reported.

2.CRYSTAL GROWTH

L-Threonine, commercially available AR grade, doubly distilled water and a dopant copper sulphate (CuSO4) were used to prepare the supersaturated solution in accordance with the solubility data available in the literature at an ambient temperature of 350C. In the present study, pure and Cu doped L-Threonine crystals were grown from aqueous solutions of various dopant concentration ratio viz.1:0.001, 1:0.002, 1:0.004, 1:0.008 and 1:0.01. Totally six crystals (one pure and five doped) were grown at identical conditions by slow evaporation technique. For the sake of convenience, the crystals prepared with dopant concentrations 1:0.000, 1:0.001, 1:0.002, 1:0.004, 1:0.008 and 1:0.010 are called as SA1, SAC1, SAC2, SAC3, SAC4, SAC5 in the forthcoming sections. About 20mm length and needle shaped crystals were grown in c- direction. All crystals are in good quality and transparent. The photograph of the Pure and Cu doped L-Threonine crystals are shown in Figure.1.

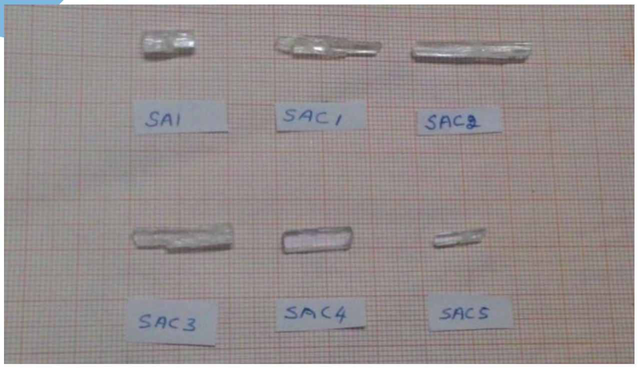

Figure 1 Photograph of Pure and Cu doped L-Threonine Crystals

3. Characterization

3.1 Density

The density of the six crystals was determined by floatation technique. The ethanol of density 0.789gm/cc and bromoform of density 2.890gm/cc were the liquids used as lower and higher densities respectively. The density of pure L-Threonine was perfectly matched with the literature value [14]. The density of the crystals can also be calculated from the crystallographic data using the well defined expression [15].

$$\rho = \frac{MZ}{NV}$$

Where, M is molecular weight; Z is number of atoms in unit cell (Z=4 for L-Threonine), N is Avogadro number; V is Volume of the Unit cell. The densities of the doped crystals are greater than pure crystal. This confirms the incorporation of dopants in the host lattice. The densities of the crystals are tabulated in table 1.

Table 1. Density of the crystals

System	Density (experimental)	Density (calculated)
SA1	1.461 [1.437]	1.468
SAC1	1.465	1.463
SAC2	1.469	1.466
SAC3	1.462	1.462
SAC4	1.466	1.464
SAC5	1.470	1.466

3.2 EDX spectrum

The dopant concentration of the crystals was estimated from the data of the EDX spectrum. The estimated concentration was matched with actual concentration of the Cu dopants. Hence, the EDX spectrum confirms the ingestion of dopant atoms into the host lattice. The EDX spectrum taken for SAC4 is shown in figure 2.

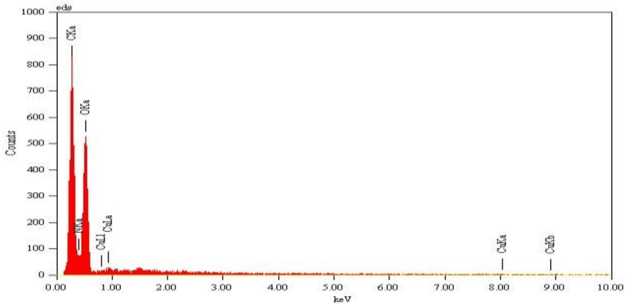

Figure 2. EDX Spectrum of SAC4

3.3 FT-Raman Spectrum

Raman spectrum was recorded for all six crystals by the Raman spectrometer (model. inVia micro Raman spectrometer, Renishaw, UK: 514 nm argon ion laser; 100%=50 mW; 50X objective Collection (Acquisition) time: 10 sec) over a range of 4000 –10 cm^{-1}. FT-Raman spectrum of SAC2 is shown in figure 3.

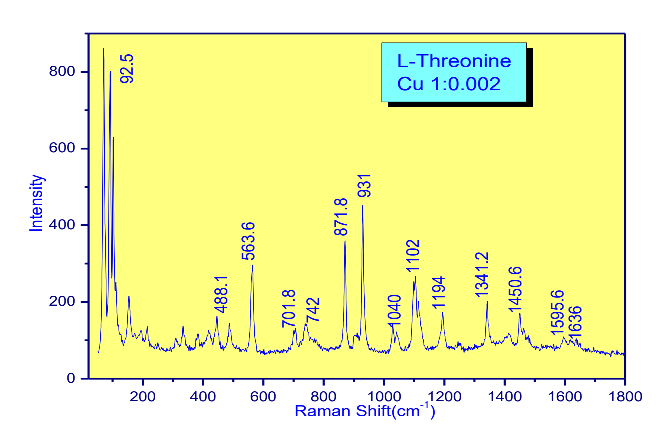

Figure 3.FT-Raman Spectrum of SAC2

The modes with low wave numbers are related to external, liberational and rotational modes and certainly are compressed torsion of CC structure, bending of CCC structure, among others [16]. The band observed at 488 $cm^{-1}$was assigned as a torsional mode of NH3. The wave number 563.8 cm^{-1} was tentatively assigned to rocking of CO_{-2} and the intensity is greater than the intensity of torsional mode of NH3 as observed in L-analine. The band with wave number 701.4cm-1 was due to wagging vibration of CO_{-2}.The band at 742.7 was assigned as torsion of COH structure [17].The intense band observed at 871.5 was related to a stretching band of CCN structure [18]. The wave number 930 cm^{-1} was assigned as CC stretching vibrations. The band at 1040 cm^{-1} was related to stretching vibration of CN. The band at 1095 cm^{-1} was possibly due to the asymmetric stretching of CCN. The rocking of NH3 was observed at 1193.9 cm^{-1}. The bending vibration of CH3 was observed at 1341.7 cm^{-1}.The wave number 1450 cm−1was assigned to the symmetric bending of NH3.The asymmetric bending of CO2 and NH3 modes were observed at wave numbers 1595.8 cm^{-1} and 1636 cm^{-1} respectively [19]. The FT-Raman pattern of the crystals confirms the formation of both L-Threonine and copper ions doped L-Threonine crystals in the present study. Raman spectrum of SAC2 is shown in figure 3.

3.3 Single Crystal X-ray diffraction

Single crystal X-ray diffraction data was collected with the help of Nonius CAD4/MACH 3 and Bruker Kappa Apex II single crystal diffractometer. The unit cell parameters, crystal system and space group of all the grown crystals were collected from single crystal X-ray diffraction and the values are provided in the table 2. It was confirmed that the structure of the grown crystals is face centred orthorhombic. The values of the lattice parameters are in well agreement with the values reported in the literature [20].

Table 2.SXRD lattice Parameters

System	a(Å)	b(Å)	c(Å)	v(Å)^3	Crystal system and Space group
SA1	5.140	7.738	13.546	538.800	Z=4
SAC1	5.140	7.728	13.610	540.660	Orthorhombic
SAC2	5.118	7.743	13.615	539.500	$P2_12_12_1$
SAC3	5.146	7.716	13.624	540.970	$\alpha=\beta=\gamma=90^0$
SAC4	5.147	7.735	13.570	540.260	
SAC5	5.144	7.723	13.585	539.600	

3.5 Powder X-Ray diffraction

The powder X-ray diffractometer data was collected for all grown crystals. The indexing was done for PXRD spectra of all the crystals using the Lipson and Steeple [21] procedure. The indexed PXRD spectrum for SAC4 is given in the figure 4. The PXRD values of the lattice parameters of pure and doped L-Threonine were closely matched with the standard SXRD L-Threonine values. The values of the lattice parameters were in well agreement with the reported values of L-Threonine [22-23]

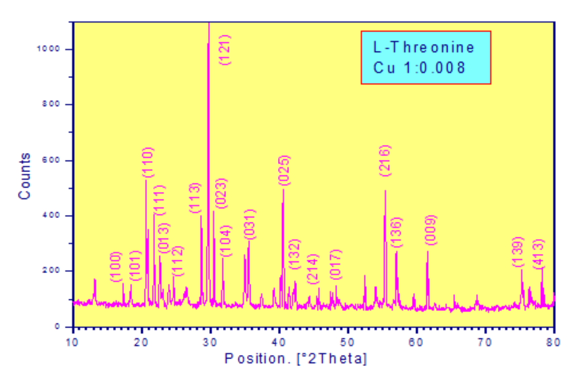

Figure 4. PXRD of SAC4

3.6 Atomic Force Microscopy

The Morphological studies were done on pure and a crystal with 0.01 dopant concentration. The two dimensional image of SA1and three dimensional image of SAC5 are shown in the figures 5 and 6. The values of arithmetic mean deviation of the roughness (R_a), root square mean deviation of the roughness (R_q), maximum peak height of roughness (R_p), maximum height of the roughness (R_z), skewness of the roughness (R_{sk}) and kurtosis of the roughness (R_{ku}) for the two crystals were obtained from atomic force microscopy. It was observed that the all values roughness parameters of doped crystal vary with the values of pure crystal. Hence it was confirmed that the morphology of the crystal changes due to doping

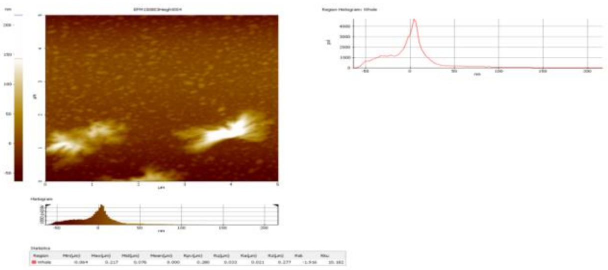

Figure 5. **AFM 2D image of SA1 crystal**

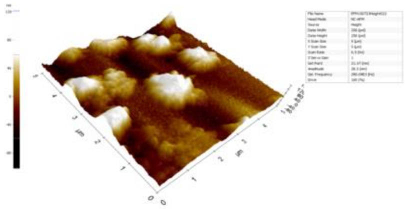

Figure 6. AFM 3D image of SAC5 crystal

3.7 Dielectric studies

Dielectric constant and dielectric loss measurements were carried out at different frequencies Viz. 1 KHz, 10 KHz, 100 KHz, 1 MHz and 2 MHz for various temperatures ranging from 40°C to 130°C using Agilant 4284A LCR meter. The variation of dielectric constant with temperature for different frequencies for SAC3 crystal is shown in the figure 7.

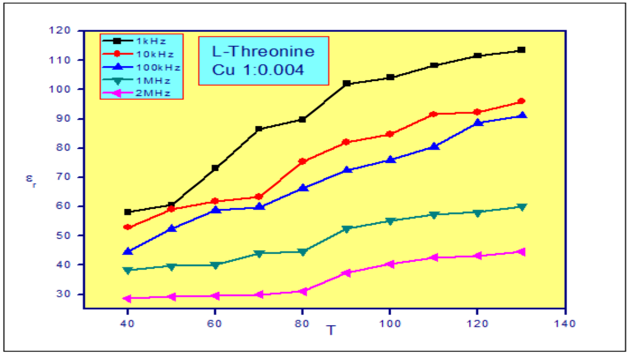

Figure 7. Variation of dielectric constant with T for SAC3

The high value of dielectric constant may be due to the presence of all the polarizations namely, space charge, orientational, ionic, and electronic polarization [24]. Of all these polarization only space charge is active at lower frequencies and there is loss of significance of other three polarizations which may lead to low value of dielectric constant at higher frequencies [25].Therefore at low frequencies, dielectric constant increases due to space charge polarization of molecular dipoles [26, 27]. As the higher frequency increases, a point will be reached where the space charge cannot sustain and comply with external field and hence polarization decreases, giving rise to diminishing values of dielectric constants. The dielectric constants at low frequency are comparable to optical frequencies which lead to minimization of a phase mismatch between electrical and optical pulses in high speed travelling wave devices. The dielectric constant for L-Threonine is less than that of other amino acid family crystals. The low dielectric constant of the L-Threonine crystal yields a low RC time constant, thus permitting a large operating band width (> 10 GHz) modulation [28, 29]. The electro optic coefficient is directly proportional to the dielectric constant of the material [30]. The variation of dielectric loss (tan δ) with temperature for SAC3 is shown in the figure 8.

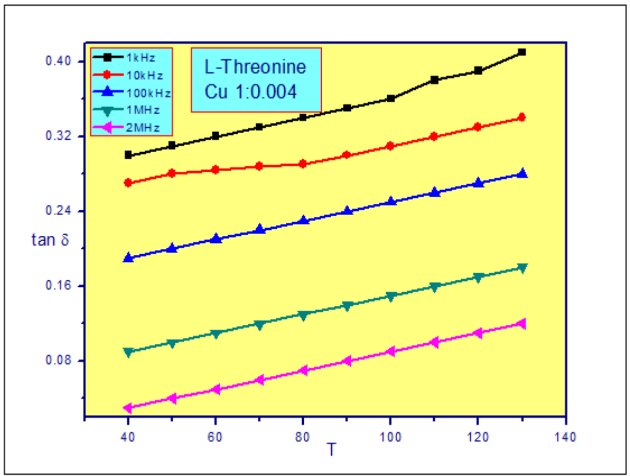

Figure 8. Variation of dielectric loss with T for SAC3

The dielectric loss decreases with increase of frequency. It is low for high frequency for all the crystals. The variance of dielectric loss is similar to dielectric constant. This behaviour enhances the crystals as the potential candidate for photonic, laser and other NLO devices [31].

The a.c. conductivity is found to increase with the increase in frequency at all temperatures for all crystals up to 1 MHz and it falls down at 2MHz for higher dopant concentration. The activation energy for SAC5 is 0.2734eV.

UV-Vis-NIR spectroscopy

The UV-Vis absorption spectra for all the samples were recorded and the spectrum of SAC2 is shown in figure 9. The figure shows that for all the crystals the lower cut off wave length is 220 nm. Hence the crystals can be used for laser applications [32]. The lower cut off wave length enhances the usefulness of the crystals in opto-electric applications and it is essential parameter for NLO applications [33].

The crystals are found to be transparent in the region of 400-800nm which is essential parameter for frequency doubling applications [34]. The minimum absorption even at NIR region makes the crystals one among the potential candidates for NLO applications [35].

The lower absorption in the entire region with a cut off 220nm was a parameter for second, third harmonic generation and other optical applications [36].

There was no remarkable absorption in the entire region, up to 1500nm. This was an important requirement for NLO materials for possible applications [37].It was observed that the crystals has high transmittance in the entire UV-Vis-NIR region and makes it suitable for opto electronic application [38].

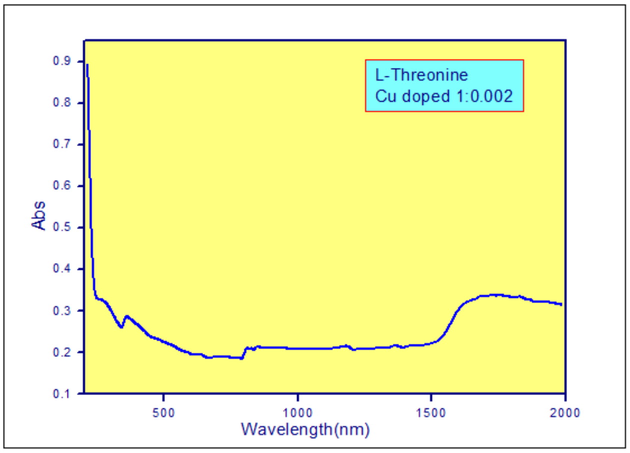

Figure 9.UV absorption graph of SAC2

3.8.1. Determination of Optical band gap and optical constants

The band gap was estimated by Tauc's plot in which $(\alpha h\nu)^2$ is plotted against hν for all crystals. Tauc's plot of SAC3 is depicted in figure 10. The band gap $E_g = 5.2$ is sustainable for LED fabrication and laser generation [31]. The high value of optical band gap suggested that the grown is dielectric in nature which can induce polarization to exhibit NLO property [39].The band gap energy was same (5.2eV) for all crystals except 0.002 Cu doped crystals (5.4eV). The wide band gap of the crystals confirmed the large transmittance in the visible region [40]. There was no significant influence in the value of band gap due to doping of copper ions. It was found that the extinction coefficient decreases with increase in photon energy. Hence the decay or damping of the amplitude of the incident electric and magnetic fields considerably decreases with increase in photon energy. The doping of copper ions had a significant impact on extinction coefficient. It varies non-linearly with dopant concentration. It is confirmed that the absorption coefficient increases with increase of photon energy. The doping of copper ions had a significant impact on absorption coefficient. It varies non-linearly with dopant concentration.

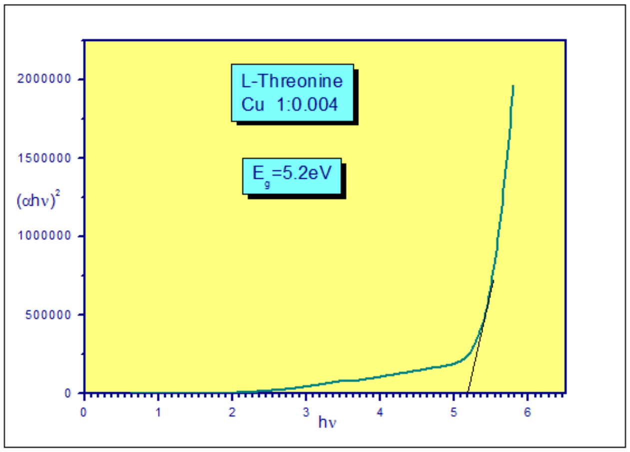

Figure 10. Tauc's Plot for SAC3

3.9 Second Harmonic Generation by Kurtz Powder Technique

All six grown single pure and Cu doped crystals were subjected to SHG efficiency study. The SHG efficiency increased with increase of dopant concentration. Hence the ingestion of copper ions has a positive impact on Second Harmonic Generation efficiency. The SHG efficiency is 2.7 times that of KDP for a 0.008 Cu doped crystal.

4. Conclusion

The grown crystals are transparent and stable. From the SXRD data, it was confirmed that the structure of the grown crystals are face centred orthorhombic and the space group is P212121. The various functional groups were elucidated by FT-Raman spectrum. The dopant concentration was estimated from EDX spectrum. The all roughness parameters obtained from Atomic Force Microscopy increase with increase of dopant concentration. Hence it is confirmed that the morphology of the crystal changes due to doping. The dielectric constant and dielectric loss increase with increase of temperature and decrease with increase of frequency. The wide band gap of the crystals confirms the large transmittance in the visible region. The SHG efficiency is 2.7 times that of KDP for a 0.008 Cu doped crystal.

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6. References

[1] G.Ramesh Kumar, S. Gokul Raj, R.Mohan, and R.Jeyavel, Journal of crystal Growth 275(2005) e1947-e1951
[2] J.J.Rodrigues Jr. et.al. optical materials 22 (2003) 235-240.
[3] Roel Baets, Photonics: An ultra-small silicon laser, Nature 498 (2013) 447-448.
[4] Redrothu Hanumantharao, S.Kalainathan Spectrochimica Acta Part-A 94(2012) 78-83
[5] Tanusri Pal, Tanusree Kar, Gabriel Bocelli and Lara Rigi., Crystal growth & design,3, (2003-16) 13-16
[6] Armington AF,Poson H and Lipson H, J.Electron.mater., 2, (1973)127
[7] J.madhavan and Ezhilarasi, International Journal of scientific and Engineering Research, 5, (2014), issue3.
[8] D.Sabashini et al., Advances in applied science research, 4(2),(2013),238-242
[9] G.Ramesh kumar et al.,9, (2008)1405-1409
[10] S.Kalainathan et. al., International Journal of Chem.Tech.Research, ,4, (2012)1478-14784
[11] Ramesh Kumar et. Al., Advances in material science and engineering.,(2009) Article Id 704294
[12] R.Umamaheshwaria., A.Joseph arul pragasama, Indian Journal of research, 2 (2013) 11,
[13] S.Masilamani., et. Al., Arabian Journal of Chemistry.,vol. 10 (2017) S3962-S3966.
[14] G.Ramesh Kumar et. al. 267, (2004)213-217.
[15] Alagar,M, Krishnakumar, R.V., Subha Nanthini, M, Natarajan, S. Acta Crystallogr.,E57, (2001)0855-0857.
[16] C.H.Wang and R.D.Stroms, J.Chem. Phys.55,3291 (1971)
[17] H.Susi, D.M. Byler and W.V.Gerasimowicz, J.Mol. Struct. 102,63 (1983).
[18] A.R. Gargaro, L.D.Barron and L.Hecht, J.Raman Spectrosc. 24, 91 (1993).
[19] P.T.C.Freire et al. Brazilian Journal of Physics, vol.28, no.1, (1998).
[20] R.L.Clark, John Krc. Jr., Anal.Chem.24 (1952) 1378
[21] H.Lipson. H.Steeple.,I nterpretation of X-Ray Powder Diffraction patterns., Macmilan ,Newyork, 1970
[22] G. Ramesh Kumar et al. Journal of crystal Growth, 267, (2004),213-217.
[23] M.R.Suresh Kumar et.al. Journal of crystal Growth 286 (2006)451-456
[24] S.M.Dharmaprakash, P.Mohan Rao, J.Mater.Sci.Lett.8 (1989),1167-1168.
[25] B.K.Singh,N.Sinha,N.Singh,K.Kumar,M.K.Gupta,B .Kumar.J.Phys.Chem.Solids 71 (2010) 1774-1779.
[26] G.Ramesh Kumar et.al. Materials Chemistry and Physics 108 (2008) 359-363.
[27] C.P.Smyth, Dielectric behaviour and structure, McGraw Hill, New York, 1965,P.P.132.
[28] Prasad, P.N, Williams, D.J. Introduction to Non Linear Optical effects in molecules and polymers: New York, 1991.
[29] Gokul raj, S. et.al. R.Mater.Chem.Phys.2005, 90,144.
[30] R.S.Adhav, J.Appl.Phys.39 (1968) 4095.

[31] P.Christuraj et.al., optik. International Journal for light and electron optics (2015) http://dx.doi.org/10.10.16/j.ijleo.2015.09.090
[32] J.Madhavan et al. Der Pharma Chemica, (2011) S6,637-642.
[33] P.Maadeswaran, S.Tirumalairajan, J.Chandrasekaran, Optik 121 (2010) 773-777.
[34] S.A.Roshan et al. Matter.Lett.49 (2001) 299-302.
[35] G.Ramesh Kuamr et al. Journal of crystal growth 283(2005) 193-197.
[36] Arun K.J. and Jayalakshmi, J. Min. Mater. Charact.Eng.8,635.
[37] S.Natarajan et al. Optik 125(2014)2505-2508.
[38] A.P.Raj et al. Optik 124(2013)6887-6891.
[39] J.Elberin Mary Theras et al. Journal of crystal growth, http:// dx. doi .org/ 10. 1016/ j. jcrysgro. 2015.06.009
[40] D.D.O.Eya, A.J.Ekpunobi, C.E. Okeke, Acad.internetJ.17(2006).