Linear and Non Linear Optical Properties of a Zinc Doped L-Threonine Single Crystals

S. Antony Dominic Christopher[1], Dr. N.Neelakanda Pillai[2]
[1]*Senior Lectrurer, Noorul Islam Polytechnic College, Punkarai, Thiruvithancode Post, Tamil Nadu, India.*
[2]*Associate Professor, Aringnar Anna College, Aralvaimozhi Post, Tamil Nadu, India*

***Abstract*: Growing non linear optical crystal is a fascinating research field today. Organic crystals have very high Second Harmonic Generation efficiency. In this view Zinc Sulphate doped L-Threonine single crystals were grown by slow evaporation technique in this study. The grown crystals were characterized optically by recording UV-Visible spectral study. The refractive index of the grown crystals are experimentally determined by Abbe's refractometer. The optical band gap energy was determined from Tauc plot. The extinction coefficient, complex optical dielectric values and optical conductivity were also determined. A Cole-Cole plot were drawn between the complex dielectric. The single oscillator energy E_o and E_d also been determined. The SHG efficiency was also determined.**

***Key words*: [UV –Visible, Tauc plot, band gap energy, optical dielectric constant , single oscillator energy and SHG efficiency]**

I. INTRODUCTION

The recent progress in laser micro mating, photo chemistry and super high resolution photo emission spectrometer urgently requires a coherent light wavelength below 200 nm in deep ultraviolet (deep UV) spectral region. Scientists in these areas are in favorite of all solid state lasers for their narrow band width, good beam quality and compact structure. The deep UV coherent light is generated through cascaded frequency conversion, using non linear optical (NLO) crystals[1]. To achieve this target, high performance deep UV NLO crystals are necessary. These crystals should possess relatively large second harmonic generation SHG coefficient and moderate birefringence [2].

The interesting physical properties of L-Threonine are high non linearity, high laser damage threshold and low refractive indices. The optical property displays some specific features such as wide transparency range in the Visible and UV spectral region and favors crystal hardness. These properties are useful for applications in the field of telecommunication, optical information storing devices and potential materials in laser system [3-6].

In this paper, optical UV-Vis- spectra were recorded and the optical properties like refractive index, optical band gap energy, optical conductivity, optical complex dielectric constant were determined and the Cole-Cole plot were drawn between complex dielectric constants and the obtained results were discussed. The SHG efficiency of the grown crystals were studied.

II. EXPERIMENTAL DETAILS

Pure and Zinc sulphate doped single crystals of L-Threonine were grown from the aqueous solution by slow evaporation technique. Totally six crystals (1 pure and 5 doped in the dopant ratio 1:0.002Zn, 1:0.004Zn, 1:0.006Zn, 1:0.008Zn, and 1:0.010Zn) were grown in identical conditions. The grown crystals were optically characterized by recording UV-Vis absorption spectra using Varian Carry 5E, UV-Vis-NIR Spectro Photometer.

The ratio of radiant power transmitted (P) by a sample to the radiant power incident (P_0) on the sample is called transmittance (T).

$$T=\frac{P}{P_o} \quad \text{But} \quad P= P_o e^{\alpha t}$$

$$\therefore T=e^{\alpha t} \quad \text{_____ (1)}$$

Where t is the thickness and α is the optical absorption coefficient, which can be calculated from the measured absorbance (A) and thickness of the film [7,8].

$$\alpha = 2.303 \frac{A}{t} \quad \text{_____ (2)}$$

The reflectance of the crystal has been found from Transmittance (T) and absorption (A) using the relationship[9].

$$R=1-(T+A) \quad \text{_____ (3)}$$

At normal incidence, the relation between refractive index (n) of the crystal and reflectance (R) are given by the formula

$$R=\frac{(n-1)^2}{(n+1)^2} \quad \text{_____ (4)}$$

The above equation can be inverted and use the reflectance and transmittance at normal incidence for given wavelength to determine the refractive index. The real part of the refractive index (n) can be determined by

$$n=\frac{(1+\sqrt{R})}{(1-\sqrt{R})} \quad \text{_____ (5)}$$

the optical energy gap E_g can be calculated from the well-known quadratic equation[10] which is often called Tauc Law.

$$\alpha h\nu = A(h\nu - E_g)^n \quad \text{_____ (6)}$$

where, $h\nu$ is incident photon energy, α is Absorption coefficient, E_g is band gap of the material, A is constant that depends on the electronic transition probability and n is an exponent that characterizes the types of electronic transition responsible. To determine the possible transitions $(\alpha h\nu)^n$ verses $h\nu$ were plotted and the corresponding band gap were obtained from extrapolating the straight portion of the graph on $h\nu$ axis to zero.

The optical conductivity σ is obtained using the relation [11]

$$\sigma = \frac{\alpha nc}{4\pi} \quad \text{_____ (7)}$$

Where 'c' is the velocity of light in space, 'n' is the refractive index and 'α' is the absorption coefficient.

A widely used graphical representation of frequency-dependent complex dielectric functions

$$\varepsilon(\omega) = \varepsilon_r(\omega) - i\varepsilon_i(\omega) \quad \text{_____(8)}$$

for various materials is the well known Cole-Cole plot [12] in which ε_i is plotted on the vertical axis against ε_r [13].

The real (ε_r) and imaginary (ε_i) part of optical complex dielectric constants can be determined using the relation [11]

$$\varepsilon_r = n^2 - k^2 \quad \text{_____9)} \quad \text{and}$$

$$\varepsilon_i = 2nk \quad \text{_____ (10)}$$

Where 'n' is the refractive index of the crystal and 'k' is the extinction coefficient given by[11]

$$K = \frac{\alpha\lambda}{4\pi} \quad \text{_____ (11)}$$

where λ is the wavelength of the incident light

The real σ_r and imaginary σ_i components of optical conductivity are described as [14]

$$\sigma_r = \omega\varepsilon_i\varepsilon_0 \quad \text{_____(12)} \quad \text{-} \quad \text{and}$$

$$\sigma_i = \omega\varepsilon_r\varepsilon_0 \quad \text{_____ (13)}$$

Where ω is the angular frequency, ε_0 is the free space dielectric constant. The free space $\varepsilon_0 = n_0^2$; The ε_0 can be determined from the static refractive index n_0 which can be determined by extrapolating the curve $\lambda \to \infty$

The dispersion parameters were evaluated according to the single effective oscillator model using the following relations [15,16].

$$n^2\text{-}1 = [E_d E_0 / (E_0^2 - (h\nu)^2)] \quad \text{_____ (14)}$$

The physical meaning of the single oscillator energy E_0 is that it stimulates all the electronic excitation involved and E_d is the dispersion energy related to the average strength of the optical transition [14], which is the measure of the intensity of the inner band gap. By plotting the graph between $(n^2-1)^{-1}$ along y axis and $(h\nu)^2$ along X-axis. The E_0 and E_d values can be determined from the slope of the best fit gives the value of (E_o . E_d) intercept gives the value of $\left(\frac{E_0}{E_d}\right)$. According to the single oscillator model, the single oscillator parameters E_0 and E_d are related to the imaginary part of the complex dielectric constant.

Based on the single oscillator model, the moment of optical spectra M_{-1} and M_{-3} can be determined by using the relation[17,18].

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \quad \text{and} \quad E_d^2 = \frac{(M_{-1})^3}{M_{-3}} \quad \text{_____ (15)}$$

The SHG efficiency of all the grown crystals were determined by Kurtz-Perry powder technique by using Quanta ray model LAB 1710-10 model HG 4 Bhigh efficient. Nd YAG laser was used in the study.

III. RESULTS AND DISCUSSION

The photograph of the given crystals are shown in figure 1. It can be observed that the given crystals are transparent and needle shaped.

Table 1. Atomic % and Estimated concentration of grown crystals

System	Actual Concen-tration	Atomic %				Estimated Concen-tration
		C	N	O	Zn	
SAZ 1	**0.002**	**72.64**	**15.97**	**11.38**	**0.01**	**0.002**
SAZ 2	**0.004**	**56.06**	**25.64**	**18.28**	**0.01**	**0.00314**
SAZ 3	**0.006**	**63.48**	**24.25**	**12.25**	**0.02**	**0.0047**
SAZ 4	**0.008**	**62.60**	**21.08**	**16.29**	**0.03**	**0.007**
SAZ 5	**0.010**	**65.58**	**18.91**	**15.47**	**0.04**	**0.0097**

Table 2. Values of Density and refractive index of grown crystals

System	Density	Refractive index
Pure	**1.30**	**1.7909 [1.654] [19]**
1:0.002 Zn	**1.3623**	**1.9163**
1:0.004 Zn	**1.3079**	**1.8112**
1:0.006 Zn	**1.3797**	**1.9216**
1:0.008 Zn	**1.3503**	**1.9138**
1:0.010 Zn	**1.3381**	**1.8518**

Fig.1: Photograph of all the grown crystals

The estimated concentration from Edas the density and refractive index are given in table 1 and 2.

The UV abortion spectrum of 1:0.002 Zn doped L-Threonine is shown in figure 2 for illustration. The UV–Visible absorption spectrum were recorded in the range 200nm to 800nm. From the spectrum, it is observed that the absorption percentage of L-Threonine crystals increases due to doping and consequently the transmittance of doped crystals are less than that of the pure L-Threonine crystals.

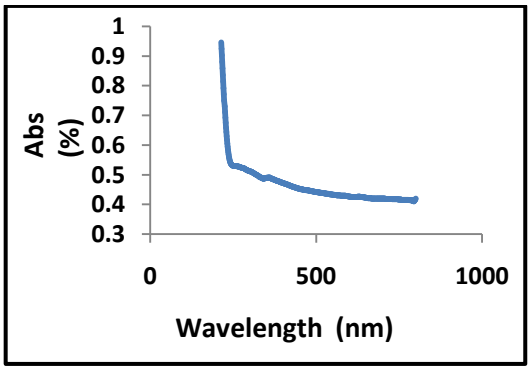

Fig .2:Variation of absorption percentage with wavelength for the crystal 1:0.002 Zn doped L-Threonine

The Tauc plot for the crystal the crystal 1:0.002 Zn doped L-Threonine is shown in figure 3 for illustration. The optical band gap energy for all the grown crystals in the present study are given in table 3.

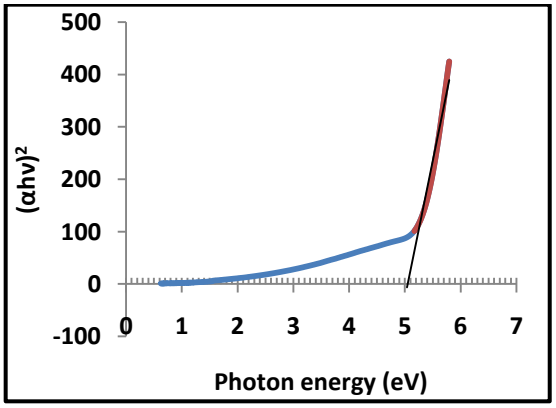

Fig.3.Tauc plot for the crystal 1:0.002 Zn doped L-Threonine.

Table 3: Values of band gap energy

System	Bandgap energy (eV)	n_0	ε_0
Pure	5.2	1.875	3.5156
1:0.002 Zn	5.1	1.725	2.9750
1:0.004 Zn	5.0	1.7	2.89
1:0.006 Zn	5.1	1.825	3.330
1:0.008 Zn	5.2	1.60	2.640
1:0.010 Zn	5.25	1.415	2.0022

It is found that the optical band gap energy of pure L-Threonine crystal is 5.2 eV. The optical energy gap of doped L-Threonine crystal in the present study are found to be almost constant. It is observed that the dopant addition has no influence on the band gap. The Tauc plot shows that the band gap is direct allowed band gap since n=2 for the equation (6).

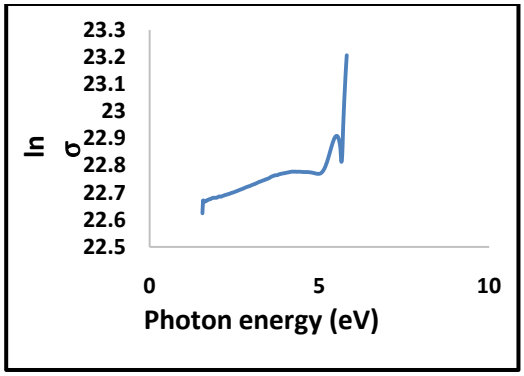

Fig .4: Variation of optical conductivity with photon energy for the crystal 1:0.002 Zn doped L-Threonine

The variation of ln σ with the incident photon energy of 1:0.002 Zn doped L-Threonine crystal is shown in figure 4 for illustration. It is observed that the conductivity increases with increase in photon energy and it is observed that optical conductivity increases abruptly after 5eV as reported by Redrothu Hanumantha Rao et al [19]. For all the samples under investigation, the optical conductivity is maximum at 5.7 eV energy. The sudden increase in optical conductivity can be attributed to the increase absorption coefficient. The high magnitude of optical conductivity of the doped crystals confirm the presence of very high photo response nature of the material. This makes the material more prominent for device application in information processing and computing. The conductivity of the doped crystals are greater than that of pure L-Threonine crystal. It reveals that the dopant addition increases the optical conductivity of the crystal. The optical conductivity of doped crystals are almost constant.

The variation of refractive index with incident wavelength of 1:0.002 Zn doped L-Threonine crystal is shown in figure. 5 for illustration. The static refractive index (n_0) values for all the crystals were determined from the curve and hence the free space dielectric constant (ε_0) can be determined. The n_0 and ε_0 values are provided in the table 3. The n_0 and ε_0 values vary non linearly with the dopant

concentration and they found to be less for Zinc doped crystals than the pure L-Threonine crystal. The graph between $(h\nu)^2$ and $(n^2-1)^{-1}$ for 1:0.002 Zn doped L-Threonine single crystal is shown in figure 6. The single oscillator energy (E_0) and (E_d) were determined from the slope and the intercept of the line of best fit of the curve. The moment of optical spectra M_{-1} and M_{-3} were also determined from E_0 and E_d values. The values of E_0,E_d, M_{-1} and M_{-3} are given in table 4. It is observed that a rapid increase in the E_0 and E_d values for the sample 1:0.008 Zn doped L-Threonine crystal when compared to other doped crystals. Since the dispersion energy E_d measures the average strength of inter-band optical transition [20]. The bound strength of the sample 1:0.008 Zn doped L-Threonine crystal is expected to be maximum which lead to increase in degree of disorder. The obtained M_{-1} and M_{-3} are both vary non linearly with concentration dopant like other optical parameters. The values are found to be low for the sample 1:0.008 Zn doped L-Threonine crystal. The optical moments are related to the macroscopic quantities like dielectric constant, effective number of valence electrons in the investigated material [21].

The variation of real part of the dielectric constant (ε_r) and the imaginary part of the dielectric constant (ε_i) with incident photon energy for the 1:0.002 Zn doped L-Threonine crystal is shown in figure 6 and 7 for illustration. It can be clearly seen from the figures, that real part of dielectric constant increases with increase in photon energy upto 5 eV except for the case of lower dopant concentration. It is almost constant upto 5eV. But the imaginary part decreases with increase in photon energy for all the grown crystals.

The graph (ε_r) versus (ε_i) for the 1:0.002 Zn doped L-Threonine crystal is shown in figure 8. It can be seen from the curve, that the curve between ε_r and ε_I fit exactly into a semi circle. At higher values ε_r, the curve diverges. On decreasing ε_r values, the imaginary dielectric constant values converge. It is the nature of semi conducting material. So, we can say the crystal grown in the present study is an optical semi- conducting material.

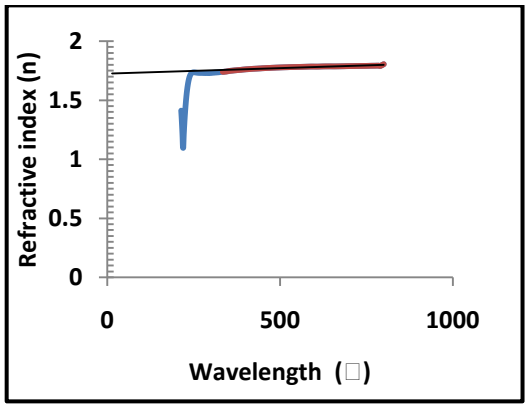

Fig.5:Variation of refractive index with wavelength for 1:0.002 Zn doped L-Threonine single crystal

Table 4 : Values of E_0 E_d, M_{-1}, M_{-2}

System	E_0	E_d	M_{-1}	M_{-3}
Pure	14.2346	21.9534	1.5422	0.0076
1:0.002 Zn	4.3997	12.6976	2.8860	0.1490
1:0.004 Zn	3.9548	12.4560	3.1496	0.2013
1:0.006 Zn	4.8532	13.9221	2.8686	0.1218
1:0.008 Zn	29.4003	42.5166	1.4461	0.0016
1:0.010 Zn	6.9959	3.8737	0.5537	0.0113

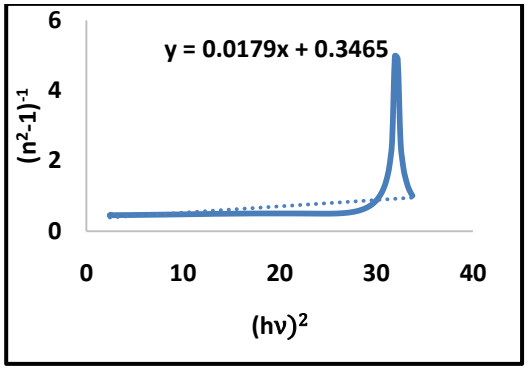

Fig.6:Graph between $(h\nu)^2$ and $(n^2-1)^{-1}$ for the crystal 1:0.002 Zn doped L-Threonine

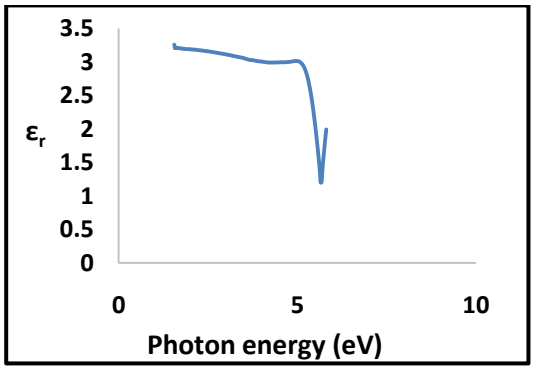

Fig.7: Variation of real part of the dielectric constant (ε_r) with incident photon energy for the crystal 1:0.002 Zn doped L-Threonine

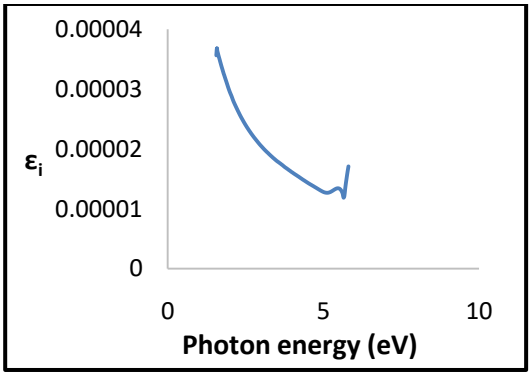

Fig.8:Variation of imaginary part of the dielectric constant (ε_i) with incident photon energy for the crystal 1:0.002 Zn doped L-Threonine

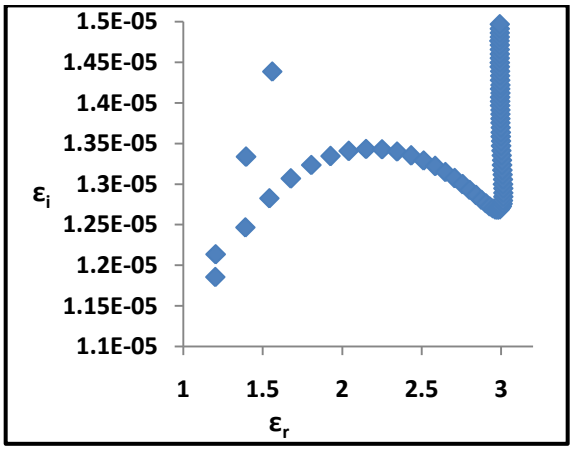

Fig.9:Cole-Cole plot between optical complex dielectric constant for the crystal 1:0.002 Zn doped L-Threonine

The variation of ln σ_i with photon energy ($h\nu$) for the 1:0.002 Zn doped L-Threonine crystal is shown in figure 9. Similarly the variation of ln σ_r with the photon energy ($h\nu$)for the 1:0.002 Zn doped L-Threonine crystal is shown in figure 10. Both increases with photon energy and reveals maximum nearly 5 eV

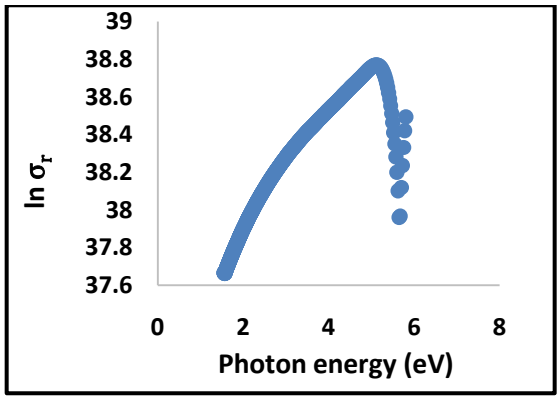

Fig .10: Variation of ln σ_r with photon energy for the crystal 1:0.002 Zn doped L-Threonine.

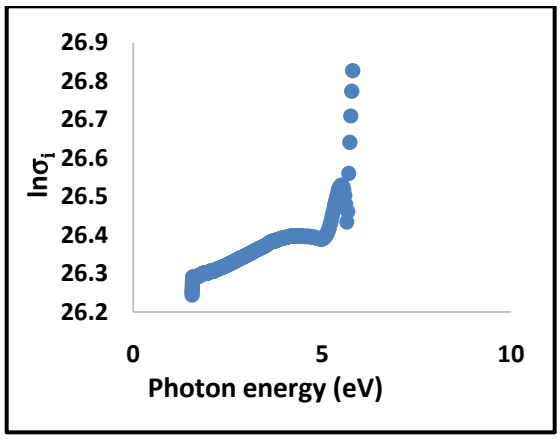

Fig .11: Variation of ln σ_i with photon energy for the crystal 1:0.002 Zn doped L-Threonine.

Table 5: Values of SHG efficiency of all grown crystals

System	SHG efficiency
Pure	**2.72**
1:0.002 Zn	**12.4**
1:0.004 Zn	**10.2**
1:0.006 Zn	**26.8**
1:0.008 Zn	**12.51**
1:0.010 Zn	**8.8**

The SHG efficiency of the grown crystal compared with KDP is provided in the table 5. It is found that, For pure L-Threonine, the SHG efficiency is less than that of KDP. For all doped crystals in the present study, the SHG efficiency is equal to or greater than the SHG efficiency of KDP. For the sample 1:0.006Zn crystal, it is three times greater than that of KDP. So the doped crystal grown in the present study exhibit very good NLO property. So these crystals can be used for photonic and opto electronic device fabrication.

IV. CONCLUSION

The Tauc plot shows the band gap is direct allowed band gap. Cole-cole plot drawn between optical complex dielectric constant fit into semi circle. Single oscillator energy E_0 and E_d shows that for 1:0.008 Zn doped L-Threonine single crystal is rapidly increased. Since the dispersion energy E_d measures the average strength of the inner band optical transition. The SHG efficiency of the sample of 1:0.006 Zn doped sample was found three times that of KDP.

ACKNOWLEDGEMENT

The authors' acknowledge to SAIF, Cochin for their help to record UV-Visible.

REFERENCES

[1]. Jones Bey.1998 (Laser focus world 34,127
[2]. Cen C.T,Ye.N, Lin.J. Jia.J,Zeng W.R and Wu B.C 1999 Adv. Matter 11,1071.
[3]. Santrana R.C,Santos M.G, Cunha. R.O., Ferreira K.D, Carvolho.J.F and Calvo R. (2007) j. phy. Chem. Solids 68,586.
[4]. Misogutti.L, Vereta. A.T,Nunes .F.D and Zilio. S.C 1996 pot matter 6,147.
[5]. Eimeri.D,Velsko.s, Davis. L, Wang. F, Laiacona. G and Kennedy G. 1989, JEEE, J.Quantum electron 25,179.
[6]. Krishnan.C, Selvarajan P., Freeda. T.H,and mahadevanC.K.2009, Physica.B 404, 289.
[7]. V.Raja.A.K.Sarma and V.V.R Narasimha Rao materials letters 57(30) 4678 -4683(2003)
[8]. J.Ballato and S.Foulger. Journal of optical society of America B 20 (9) 1838- 1843 (2003)
[9]. O.Gh. Abdullah and D.R.Sabeer. Applied mechanics and materials[110-116,177-182,(2012).
[10]. R.A. Ibrahim, S.K.Al. Ani (1994) Czechoslovak. Journal of physics , 44, 785-797.
[11]. R. Das and Pandy (2011) JJIMS.1(1), 35-40.
[12]. K.S.Cole, R.H.Cole. J.Chem.phy, 9,3 45, (1941) 10, 98.
[13]. Debye, Chemical Catalogue company (1929)

[14]. S.H.Wemple. phys, Rev, B7 (1973) 3767-3777.
[15]. S.H Wemple, Di. Domenico J.Appl.phys, 40(1969), 720-74
[16]. K.R.Tagreed, Journal of Al. Nahrain University 16 (2013) 164-170.
[17]. H.E. Atiya. Opto electron Adv,M,8,(2006) 1359-1366.
[18]. M A.Mahdi and S.K.J. Al. Ani. Int. J. nano electronics and materials 5, 11-24 (2012)
[19]. Redrothu Hanumantha rao and S.Kalainathan Int. J. Chem Tech Research Vol4. No 4, pp1478-1484 Oct-Dec 2012.
[20]. M.Modreanu,M.Gartner, N.Tomozeiu Int. J. nano electronics and materials 5, 11-24 (2012)
[21]. A.H. Ammar. Applied surface sciences 201, 1-19 (2002)