

DIRECTIONAL GROWTH OF L-GLUTAMIC ACID HYDROCHLORIDE (LGHCL) SINGLE CRYSTALS GROWN BY CONVENTIONAL AND SANKARANARAYANAN-RAMASAMY (SR) METHOD: A COMPARATIVE STUDY BY MEANS OF OPTICAL, LDT, PHOTOCONDUCTIVITY, PHOTO ACOUSTIC AND POLARIZABILITY PROPERTIES

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ABSTRACT

Growth of non-linear optical single crystals of Lglutamic acid hydrochloride by Sankaranarayana - Ramasamy (SR) method. The (001) face was chosen for unidirectional growth. The grown crystals was confirmed by single crystal X-ray diffraction (SXRD) and characterized using optical, Laser damage threshold, Photoconductivity, Photoacoustic, electronic polarizability and their properties were compared by conventional method. Results show that the SR method grown crystal exhibit higher optical, laser damage threshold, photoconductivity due to relatively high- crystalline perfection. The electronic polarizability and photoacoustic were also discussed for the title compound.

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INTRODUCTION

In the recent past decade, semi organic nonlinear (NLO) optical single crystals have emerged as one of the most attractive fields of research in view of potential applications in the area of optoelectronics, photonics, telecommunication, optical computing, optical storage and optical information process[1,2]. For practical NLO applications, the crystals must possess good optical transparency, high laser damage threshold, high mechanical strength and so on. These restrictions are satisfied by the semi organic single crystals [3]. The conventional method is mostly used for the convenience, simplicity and the possible avoidance of complex growth apparatus. There are different techniques are available to grow bulk size single crystals. The Sankaranarayanan-Ramasamy (SR) method is the best way to grow bulk size single crystal in solution technique for device applications [4]. The main advantages of SR method are simple experimental setup, unidirectional (single plane) growth, high solution-crystal conversion, minimum thermal stresses on the crystal during growth and avoidance of the microbial growth [5]. Finally, we can achieve bulk size single crystals with required specific orientation. The literature information concerning with growth and characterization of L-Glutamic acid hydrochloride (LGHCL) are reviewed here:

Bairava Ganesh *et al*, [6], Selvaraju *et al* [7], Sathyalakshmi *et al* [8] and Uma *et al* [9] reported the title compounds for UV-transmittance, mechanical, dielectric and SHG measurement. To the best of our knowledge, there are no earlier reports have encountered in the literature survey on systematic comparative investigations on photoluminescent, Laser damage threshold, Photoconductivity, Photoacoustic and electronic polarizability by conventional and SR method for LGHCL crystal.

Experimental procedure and crystal growth

L-glutamic acid hydrochloride (LGHCL) was synthesised from the raw materials of L-glutamic acid and hydrochloric acid (Fig.1) taken in stoichiometric ratio of 1:1 and water is used as a solvent [10].

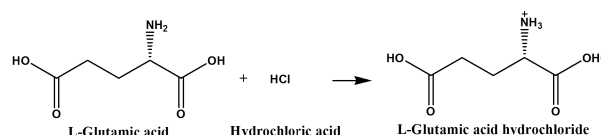


Figure 1 Reaction scheme of LGHCL

The synthesized materials have been purified by repeated recrystallization process to eliminate any impurities in the grown crystals using same solvent. The optically good transparent LGHCL crystals of size 12 x 5 x 3 mm³ were grown from conventional and it is shown in Fig.2(a). The morphology of LGHCL has been indexed by using WinXmorph software (Fig.2 (b)). Based on the morphology

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of the conventionally grown LGHCL crystal, the (001) face was selected. According to the Periodic bond chain (PBC) theory, the growth rate of crystal at particular orientation is directly proportional to attachment energy. The faces which have higher attachment energy grow faster than the other orientation (Wang Yan *et al* 2005) [11]. The fast growth orientation (001) was used for growth of large size LGHCL crystals.



Figure a

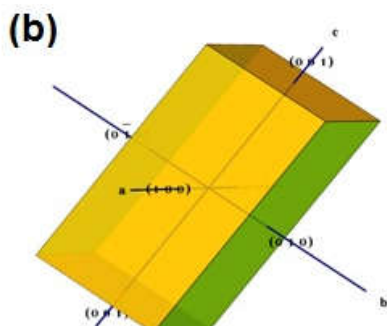


Figure b

Figure 2 (a) conventionally grown crystal and (b) Its morphology

The seed crystal was mounted at the bottom of the glass ampoule along (001) orientation. The saturated homogenous solution was prepared and transferred into seed mounted glass ampoule without any disturbance to seed and positioned in an assembled water bath. The suitable temperature was provided by the ring heater to avoid the temperature fluctuation around the ampoule. The perfect growth has been achieved by optimization of temperature. The temperature at the top of the ampoule was 40°C for solvent evaporation and at the bottom is 34°C for growing crystal. After 10 days, the mounted seed crystal started to grow at the bottom of the ampoule. Under this condition the growth system was kept undisturbed for a long period. Crystals of 130 mm in length and 20 mm in diameter have been grown successfully within a period of 60 days. The Fig.3 (a) and (b) shows the SR method grown LGHCL single crystal with the ampoule as well as cut and polished crystal wafers respectively.



Figure 3 a

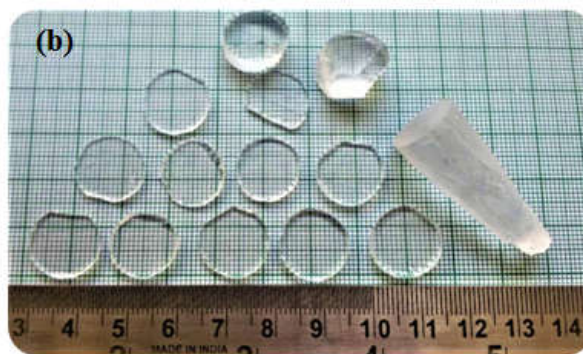


Figure 3 (a) SR method grown crystal with the glass ampoule and (b) Cut and polished LGHCL crystal

Characterization technique

The grown LGHCL single crystal was subjected to various characterization studies. The Bruker AXS Kappa APEX II CCD Diffractometer, equipped with monochromatic Mo K_{α} radiation ($\lambda = 0.710 \text{ \AA}$) was used to estimate the cell parameters. UV-Vis NIR transmission spectrum studies were carried out in the range 190-1200 nm using Perkin-Elmer Lambda-35 spectrophotometer. The photoluminescence spectrum was recorded with Shimadzu Spectrofluorophotometer R.F-5031 PC series with Xenon arc lamp as the excitation source. The conductivity behaviour was carried out on a cut and polished LGHCL sample using KEITHLEY 6487 picoammeter in the presence of DC electric field at room temperature. The photoacoustic and electronic polarizability were also determined. Laser damage threshold studies were carried out using Q-switched Nd: YAG laser operating at 1064 nm radiation.

RESULTS AND DISCUSSIONS

X-ray Diffraction

The single crystal XRD data confirms that, the LGHCL crystal belongs to orthorhombic crystal system having non-centrosymmetric nature with space group $P2_12_12_1$ and the cell parameters are $a=13.23(8) \text{ \AA}$, $b= 11.68(1) \text{ \AA}$ and $c=5.161(5) \text{ \AA}$ with Volume $V= 797.99 \text{ \AA}^3$. The observed values are in good agreement with the reported values [10].

Optical analysis

UV-Vis NIR analysis

The optical transmission spectrum gives valuable information about the band gap energy, band structure and the

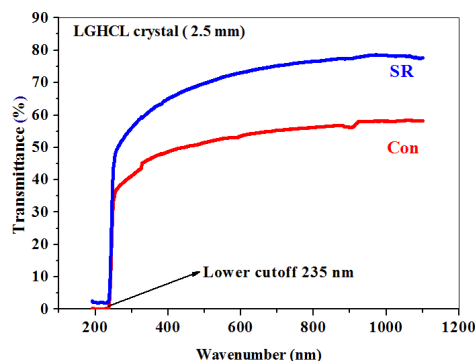


Figure 4 UV-Vis NIR spectrum of conventional and SR method grown crystals

transparency window which are very essential for the device in optoelectronic applications [12]. The transmittance spectrum was recorded in the wavelength range from 200-1100 nm and shown in Fig.4. The good and defect free sample with well-polished surface of conventional and SR grown LGHCL crystal along (001) orientation with identical thickness of 2.5 mm were employed. The LGHCL crystal has good transparency in the entire visible region. The absence of absorption of light in the visible region is an intrinsic property of all the amino acids. Absence of absorption in the entire region is the most desirable property of the materials possessing NLO activity. The cut off wavelength of both the method grown LGHCL crystal was found to be 235 nm, which is sufficient for SHG. It was observed that the transmittance percentage of SR method grown crystal was 23 % higher than that of conventionally grown crystal. This may be attributed to reduced scattering centers from point and line defects. This illustrates the optical quality of the SR method grown crystal. The optical absorption co-efficient (α) was calculated using the relation,

$$\alpha = \frac{2.3026}{t} \log_{10} \left(\frac{100}{T} \right) \quad (1)$$

where 'T' is the transmittance (%) and 't' is the thickness of the crystal (2.5 mm). In the high photon energy region, the energy dependence of the absorption co-efficient suggests the occurrence of a direct band gap of the crystal obeying the following equation

$$(\alpha h\nu) = A(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

where 'A' is a constant, ' E_g ' the optical band gap and ' $h\nu$ ' is the incident photon energy. The Tauc's graph [13] plotted between variation of $(\alpha h\nu)^2$ versus $(h\nu)$ is shown in Fig. 5. Using this graph the band gap energy E_g was calculated by extrapolating the linear portion near the onset of absorption edge to the energy axis and is equal to 5.05 eV, which is consistent with theoretically calculated value 5.2 eV using the relation $E_g = h\nu / \lambda_{max}$.

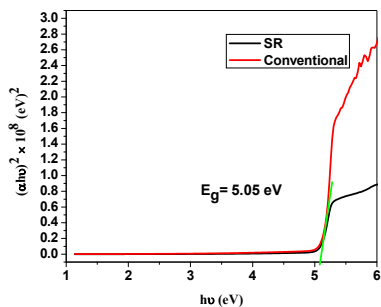


Figure 5 Band gap of LGHCL crystals

Photoluminescence (PL) measurement

The photoluminescence is highly depends on the crystallinity and structural perfection of the crystal. It is the spontaneous emission of light radiation by the absorption of photons. Although the excitation energy is typically in the form of photons, it could also be generated by an electric field or by ionizing radiation. The LGHCL crystal was excited at 300 nm and the emission spectrum was recorded in the range between

250-650 nm and shown in Fig.6. Generally, photoluminescence phenomenon is expected in aromatic molecules which contain multiple conjugated bonds leading to a high degree of resonance stability [14]. The sharp emission peak in the blue region observed at 480 nm for both conventional and SR method grown LGHCL crystal.

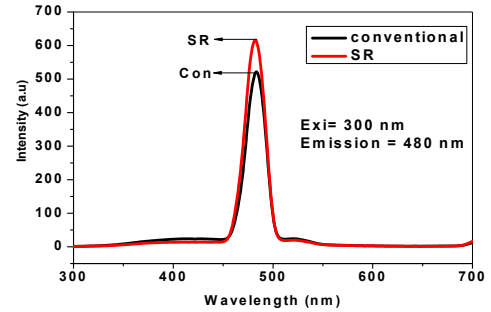


Figure 6 Photoluminescence of conventional and SR method grown crystal

The high peak intensity of the SR method grown crystal indicates its crystallinity and optical quality enrichment [15].

Laser damage threshold (LDT)

Laser damage threshold (LDT) analysis is very important because the functions of NLO devices such as second harmonic generation, electro-optic modulation, THz wave generation etc., mainly involve in the ability to sustain high intensity laser light. In the present study, a Q-switched Nd:YAG laser operating at wavelength of 1064nm with 10 Hz repetition rate and pulse width of laser 10 ns was used. The multiple shots laser damage threshold measurements were made conventional and SR method grown crystals having 2.5 mm thickness. Initially 30 mJ was applied on the (001) surface of both the crystals and then gradually increased. For SR grown crystal when the laser energy was increased up to 427mJ, a visible damage and cracks have been observed. The diameter of the damage spot was 893.04 μm , whereas for conventionally grown crystals the damage spot of diameter 1897.74 μm was observed at 388mJ. The surface damage profile as observed through the optical microscope is shown in Fig.7 (a, b). The energy density (P_d) was calculated by taking the ratio of input energy and area of the crystal exposed to laser radiation which is expressed in GW/cm^2 i.e.,

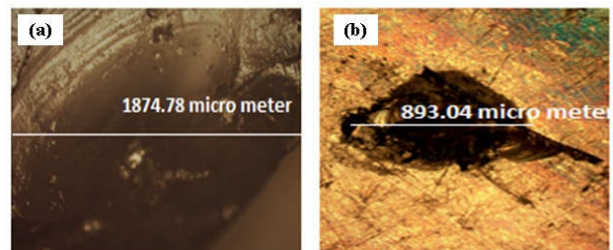


Figure 7 Laser damaged surface of (a) conventional and (b) SR method grown crystal

$$\text{Power density } (P_d) = \frac{E}{\tau \pi r^2} \quad (3)$$

where 'E' is the input energy density (mJ), ' τ ' is the pulse width (ns) and ' r ' is the radius of the damage spot (μm) on the sample. The damage threshold were

found to be 1.4 GW/cm² and 6.8GW/cm² for the crystals grown by conventional and SR method respectively. High value of LDT indicates that SR method grown LGHCL crystal contains very low defects and is in tune with less EDP of 3.1x10² cm⁻² shown in Fig. 8 (b). The low LDT value of conventionally grown LGHCL crystal suggests the high dislocation content in the crystal due to the presence of growth sector boundaries (EPD = 5.2x10² cm⁻² (Fig.8(a)). In SR method grown crystal there is no growth fluctuation/growth sector boundaries due to uniform growth rate. The calculated laser damage threshold value of LGHCL is higher than that of KDP, urea[16] and other standard NLO materials like KNbO₃, LiNbO₃[17].

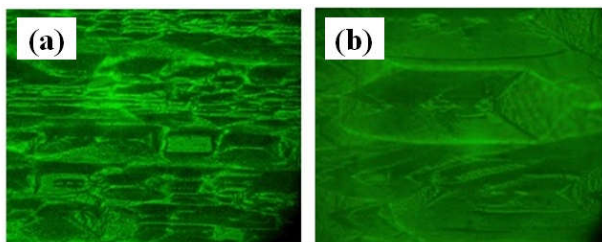


Figure 8 (a) Etch pit pattern of conventional and (b) Etch pit pattern of SR method grown crystal

Photoconductivity

When a material absorbs radiation of sufficient quantum energy there may be an increase or decrease of electrical conductivity called photoconductivity. The photoconductivity measurements of the grown LGHCL crystals were carried out at room temperature. Electrical contacts were made on the sample using silver paint and it was connected to the electrodes. The DC voltage applied to the electrodes and it was varying from 1-50 V with step voltage of 1V/s for the entire work. The light from halogen lamp of 50 W was focused on the sample.

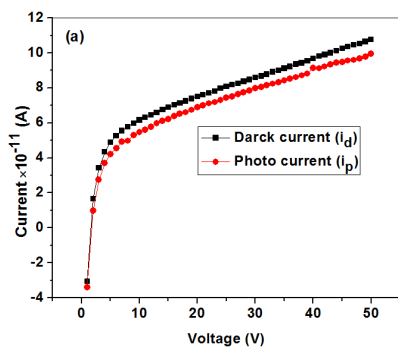


Figure 9 a

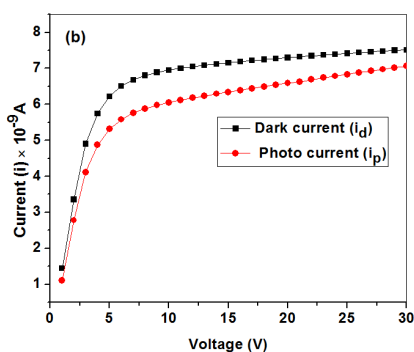


Figure 9 b

Figure 9 Photoconductivity of (a) conventionally grown crystal and (b) SR method grown crystal

Initially the dark current (i_d) was recorded by keeping the sample unexposed to any radiation with respect to the applied voltage. As well as photocurrent (i_p) was measured by applying the same voltage under illumination. Fig.9 (a) and (b) shows analysis for SR and conventional method which depicts the dark current is always higher than the photocurrent, thus confirming the negative photoconductivity nature. This may be due to decrease in either the number of charge carriers or their life time, when subjected to radiation. Decrease in life time with illumination could be due to the trapping process and increase in carrier velocity according to the relation:

$$\tau = \left(\frac{1}{\nu s N} \right) \quad (4)$$

where 'v' is the thermal velocity of the carriers, 's' is the capture cross section of the recombination centers and 'N' is the carrier concentration. The phenomenon of negative photoconductivity was explained by Stockmann model [18]. The intense light continuously falls on the sample, the lifetime of the charge carriers could be decreases. As a result, the recombination of electrons and holes take place resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity. Negative photoconductivity materials can be used for UV and IR detector applications [19]. The SR method grown crystal has higher photosensitivity than the conventionally grown crystal, as its depend upon the value of I_p , which is greater for SR method grown crystal.

Photoacoustic analysis

Photoacoustic spectroscopy (PAS) is the oldest form of photo thermal spectroscopy. It is a technique or mechanism of detecting and measuring the absorption coefficient of weakly absorbing or opaque and diffuse materials. In PAS, the irradiation of the sample contained in a closed gas cell produces temperature and pressure fluctuation in the gas which couples the light to the samples synchronous with the modulated source signal. A microphone placed in the gas cell picks up these fluctuations and an associated amplifying system produces an electrical signal whose amplitude and phase monitored over a range of wavelengths contain information about a wide range of optical phenomenon including optical absorption in highly transparent materials, non-linear absorption and localized defect characteristics [20-22]. The unique advantage of PAS over other conventional spectroscopy is that it does not require optical detection of either transmitted or reflected.

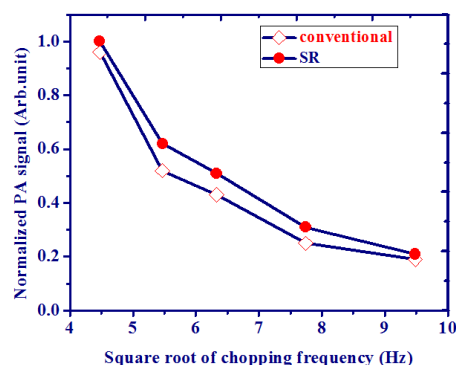


Figure 10 Photoacoustic study for conventional and SR method grown crystal

The variation of photo acoustic signals with respect to chopping frequency from 20 to 90 Hz was measured for both the crystals. The normalised spectra of PA signal versus square root of chopping frequency are shown in Fig.10. The thermal diffusivity is an important parameter for NLO material that describes the heat transport from the hot side to cold side. From PA analysis, the thermal diffusivity was derived by curve fitting method adopted by Barros and Mela [23]. The Fig.10 it illustrates, the conventionally grown crystal has lower thermal diffusivity value due to its crystalline defects.

Electronic polarizability (α)

The parameter of electronic polarizability (α) of the material is essential for desired efficiency of nonlinear effect. Theoretically the valence electron Plasma energy, Penn gap, Fermi energy and electronic polarizability are depends upon the dielectric constant. The valence electron plasma energy ($\hbar\omega_p$) is given by [24]

$$\hbar\omega_p = 28.8 \left(\frac{Z' \times \rho}{M} \right)^{\frac{1}{2}} \tag{5}$$

where the total number of valence electrons of LGHCL crystal is $Z' = [(5 \times Z'_c) + (10 \times Z'_H) + (1 \times Z'_{cl}) + (1 \times Z'_N) + (4 \times Z'_O)] = 66$. 'M' the molecular weight and 'ρ' is the density of LGHCL.

According to the Penn model [25], the average Penn gap (E_p) and Fermi energy (E_F) for LGHCL are calculated using the following relations:

$$E_p = \frac{\hbar\omega_p}{(\epsilon' - 1)^{\frac{1}{2}}} \tag{6}$$

$$E_F = 0.2948(\hbar\omega_p)^{\frac{1}{2}} \tag{7}$$

where ϵ' is the dielectric constant. The dielectric constant for the SEST and SR method grown crystals are 50 and 55 respectively. The electronic polarizability (α) of the LGHCL crystal are calculated using the following relation [26]

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \tag{8}$$

where, 'S₀' is a constant for a particular material which is given by

$$S_0 = 1 - \left[\frac{E_p}{4E_F} \right] + \frac{1}{3} \left[\frac{E_p}{4E_F} \right]^2 \tag{9}$$

The value of electronic polarizability (α) is also confirmed by using the Clausius-Mossotti relation:

$$\alpha = \frac{3M}{4\pi N_A \rho} \left(\frac{\epsilon' - 1}{\epsilon' + 2} \right) \tag{10}$$

For SR grown crystal, the electronic polarizability is two times greater than that of KDP [27]. The calculated parameters are shown in Table 1.

Table 1 Electronic polarizability (α) results based on dielectric analysis

Parameters	Conventional	SR	KDP [27]
Plasma energy $\hbar\omega_p$ (eV)	21.179	21.179	17.33
Penn gap energy E_p (eV)	3.025	2.462	2.39
Fermi energy E_F (eV)	17.274	17.274	12.02
Electronic polarizability (α) using Penn analysis (cm ³)	4.542×10^{-23}	4.637×10^{-23}	2.14×10^{-23}
Electronic polarizability (α) using Clausius-Mossotti equation (cm ³)	4.560×10^{-23}	4.650×10^{-23}	2.18×10^{-23}

CONCLUSIONS

The optically transparent semi-organic NLO single crystal of L-Glutamic acid hydrochloride (LGHCL) has been successfully grown by conventional method using water as solvent. High quality (001) directed LGHCL crystal of dimension 130 mm long and 20 mm diameter was successfully grown by Sankaranarayanan-Ramasamy (SR) method. The lattice parameter values were determined from the single crystal XRD and it is shown that it belongs to orthorhombic crystal system with the space group P2₁2₁2₁. Transmission spectral analysis shows that the transmittance percentage of SR grown crystal was 23% higher than that of conventionally grown crystal. The observed high intensity in the blue region for SR method grown crystal, indicates its high crystalline perfection and outcome compared to conventionally grown crystal. The laser damage threshold studies indicate that the SR method grown crystal has good optical tolerance due to its crystalline perfection. Though both the crystal exhibits negative photoconductive nature, the photosensitivity is greater for SR method grown crystal. Higher thermal diffusivity in SR grown crystal is a favourable property for NLO materials, since the heat dissipation is faster during high power laser irradiation.

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References

1. D. Wang, G. Zhou, X. Xu, X. Wang, H. Liu, Y. Ren, Z. Shao, M. Jiang, *Opt. Laser Technol.* 34 (2002) 343-346.
2. J. Badan, R. Hierle, A. Perigaud, J. Zuss (Eds.), American Chemical Symposium Series 233, American Chemical Society, Washington. DC, 1993.
3. H. Q. Sun, D. R. Yuan, X. Q. Wang, X. F. Cheng, C. R. Gong, M. Zhou, H. Y. Xu, X. C. Wei, C. N. Luan, D. Y. Pan, Z. F. Li, X. Z. Shi, *Cryst Res Technol.* 40 (2005) 882-886.
4. F. Barati, H. RezagholipourDizaji, *Opt. Quant. Electron* (2016) 48:432.
5. R. Bairava Ganesh, V. Kannan, R. Sathyalakshmi, P. Ramasamy, *Mater. Lett.* 61 (2007) 706-708.
6. K.Sankaranarayanan, P.Ramasamy, *J. Crystal Growth* 280 (2005) 467-473.
7. K. Selvaraju, K. Kirubavathi, N. Vijayan, S. Kumararaman, *Mod. Phys. Lett. B* 23 (2009) 861-869.

8. R. Sathyalakshmi, V. Kannan, R. Bairava Ganesh, and P. Ramasamy, *Cryst. Res. Technol.* 42, No. 1, 78 - 83 (2007) / DOI 10.1002/crat.200610775
9. J. Uma, V. Rajendran, *Progress in Natural Science: Materials International* 26 (2016) 24-31
10. M. Delfino, J.P. Dougherty, W.K. Zwicker, M.M. Choyk, *J. Cryst. Growth* 36 (1976) 267-272
11. Wang Yan, Yu Xi-ling and Yin Shao Tang, *Cryst. Res. Technol.*, Vol 40, (2005), 768-772.
12. A. L. Fahrenbruch and R.H. Bude, *Fundamentals of Solar Cells*, Academic, New York, 1983.
13. J. Tauc, R. Grigorovici, A. Vancu, *Optical properties and electronic structure of Amorphous Germanium*, *Phys. Status Solidi.* (b) 15 (1966) 627-637
14. P. Karuppusamy, V. Sivasubramani, M. Senthil Pandian and P. Ramasamy, *RSC Adv.*, 6 (2016) 109105-109123.
15. M. Parthasarathy, R. Gopalkrishnan, *J. Cryst. Growth* 372 (2013) 100-104
16. N. Vijayan, G. Bhagavannarayana, K. R. Ramesh, R. Gopalakrishnan, K. K. Maurya and P. Ramasamy, *Cryst. Growth Des.* 6 (2006) 1542-1546.
17. H.L. Bhat, *Growth and characterization of some novel crystals for nonlinear optical applications*, *Bull. Mater. Sci.*, 17 (1994) 1233-1249
18. I. M. Ashraf, H. A. Elshaikh and A. M. Badr, *Photoconductivity in Tl_4S_3 layered single crystals*, *Cryst. Res. Technol.* 39 (2004) 63-70.
19. V. N. Joshi, *Photoconductivity*; Macrel Dekker. New York, 1990
20. T. Somasundaram, P. Ganguly, and C. N. R. Rao, *Journal of Physics - C*, 19, (1986), 2137.
21. S.A. Martin Britto Dhas, E. Ramachandran, P. Raji, K. Ramachandran, and S. Natarajan, *Crystal Research Technology*, 42(6), (2007), 601 - 606.
22. P. Raji, C. Sanjeeviraja, and K. Ramachandran, *Crystal Research Technology* 39, (2004), 617.
23. W.L. Barros Melo and R. M. Faria, *Applied Physics Letter*, 67, (1995), 3892-3894.
24. J. D. Jackson, *Classical Electrodynamics*, Wiley Eastern. 1978, 321.
25. D. R. Penn, *Wave-number-dependent dielectric function of semiconductors*, *Phys. Rev.*, 128 (1962) 2093-2097.
26. C. Balarew, R. Duhlew, *Synthesis, Optical and Dielectric Properties of Tris-Glycine Zinc Chloride (TGZC) Single Crystals*, *J. Solid-State Chem.* 55 (1984) 1-6.
27. A. Dev, S. Chakrabarti, S. Kar and S. Chaudhuri, *Journal of Nanoparticle Research*, 7, (2005), 195-201

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