Nonlinear optical investigations on novel gadolinium (III) ion doped L-histidine hydrochloride single crystal by solvent evaporation method

N. POONGODI[a], P. DHANASEKARAN[b,*], N. M. GANESAN[a], T. S. SENTHIL[a]
[a]*Department of Physics, Erode Sengunthar Engineering College, Erode-638057, Tamilnadu, India*
[b]*Department of Physics, Bharathiar University Arts& Science College, Erode-638104, Tamilnadu, India*

Semi organic single crystals of gadolinium (III) ion doped L-Histidine hydrochloride was successfully grown for the first time by slow evaporation technique. The structural parameters wereobtained by single crystal X-ray diffraction spectrum. The XRD spectrum reveals the grown crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. Functional groups of the grown crystal were identified from FT-IR spectral analysis. The optical band gap and optical coefficient ofthe grown crystal were calculated by UV-Visible spectroscopy. The chemical composition of the grown crystal was confirmed by energy dispersive X-ray analysis. The thermal stability of the grown crystal was investigated by thermo-gravimetric and differential thermal analysis (TG/DTA) measurement. The second harmonic generation (SHG) efficiency for the grown crystal was measured by Kurtz Perry powder technique. The SHG efficiency of the gadolinium (III) ion doped L-Histidine hydrochloride is found to 1.2 times greater than that of pure L-Histidine hydrochloride.

(Received June 11, 2018; accepted June 14, 2019)

Keywords: Crystal growth, Rare-earth metal, Single crystal, X-ray diffraction, Optical material

1. Introduction

The search for new semiorganic nonlinear optical (NLO) materials with high optical nonlinearities is an important area due to their practical applications such as optical communications, optical computing, remote sensing, color display, medical diagnostics, etc., [1]. Most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible to damage during processing. Semiorganic NLO crystals have good thermal and mechanical properties and large nonlinear coefficients. Amino acids and strong inorganic acids are good raw materials to produce semi-organic crystals. Because, amino acid crystals possess good optical properties as they contain a proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group. Recently, many authors have grownL-Histidine halide derivatives for NLO applications [2-5]. To the best of the author's literature survey, only a few articles have been published on the combination of L-Histidine and Hydrochloric acid [6-8]. Some of the L-Histidine compounds exhibit high second harmonic generation conversion efficiency [9]. L-Histidine bromide [10], L-Histidine hydro fluoride dehydrate, tartaric acid mixed L-Histidine hydrochloride monohydrate [11] and Tb^{3+} ion doped L-Histidine hydrochloride monohydrate [12] are the semi organic materials which possess high values of SHG. In the present study, we report the growth of gadolinium (III) ion (Gd^{3+}) doped L-Histidine hydrochloride single crystal by slow evaporation technique for the first time. Slowevaporation solution technique (SEST) is the most basic and less expensive technique to grow the numerous organic, inorganic and semiorganic single crystals for many technological applications. In this technique, required supersaturation is attained by evaporating the solvent at low temperature. The growth rate and crystal quality can be controlled by controlling the solvent evaporation. An added advantage of SEST is that the prevention of major thermal shock to the grown crystal and removal of crystal from the growth apparatus. Hence, SEST has been used for the growth of Gd^{3+} doped L-Histidine hydrochloride single crystals. Rare-earth metal, gadolinium forms trivalent ions with fluorescent properties and good transparency in the UV region. It has low toxicity in biological role and its compounds are useful in magnetic resonance imaging (MRI), particularly in diagnosing cancerous tumors as well as used for making electronic components and magneto-optic recording devices. The grown crystal was characterized by single crystal X-ray diffraction, FTIR, UV-Visible spectrum, TG-DTA, EDAX and SHG studies to reveal their lattice parameters, functional groups, optical transmittance, thermal stability, presence of dopant in the crystal lattice and optical property respectively.

2. Experimental

2.1. Crystal growth

Gadolinium (III) ion doped L-Histidine hydrochloride (Gd^{3+}:LHHCl) compound was successfully grown by the solvent evaporation technique. The 1: 1 equilimolar ratio of L-Histidine (Alfa Aesar) and hydrochloric acid (Merck) was chosen as a raw materials. The conventional L-Histidine hydrochloride chemical reaction as shown below.

$$C_6H_9N_3O_2 + HCl \rightarrow C_6H_{10}N_3O_2Cl$$

The solution was stirred well, then 0.02 mole% of gadolinium (III) nitrate hexahydrate was added into the solution as a dopant. The purity of the salt was further improved by repeated recrystallization process. The saturated Gd^{3+}:LHHCl solution was prepared at 30°C and stirred well about 6 hrs using magnetic stirrer with constant 150 rpm to obtain the homogeneous mixture. The saturated solution was filtered using Whatmann No.1 filter paper to eliminate the suspended impurities. Then, it was kept in a crystallizing vessels covered with polyethylene perforated sheet and kept in an undisturbed place of atmosphere (crystallizing chamber). After a span of 24 days, a good quality transparent and colorless single crystal of $Gd^{3+:}$LHHCl was harvested as shown in the Fig. 1.

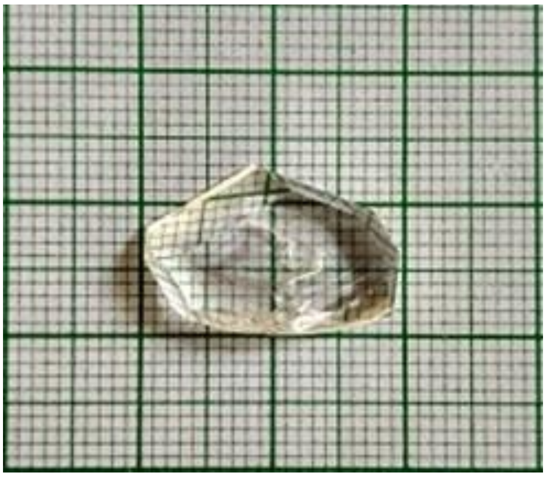

Fig. 1. Grown Gadolinium (III) ion doped L-Histidine hydrochloride (Gd^{3+}: LHHCl) single crystal

2.2. Characterization

A small specimen of Gd^{3+}: LHHCl single crystal having dimensions 0.200 mm × 0.440 mm × 0.540 mm was cut out from the grown crystal and then subjected to single crystal XRD analysis. The structure was solved by the direct method and refined by the full matrix least-squares technique using the SHELXL program. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The FTIR spectrum confirm the presence of functional groups in Gd^{3+}: LHHCl grown crystal in the frequency region between 400 and 4000 cm^{-1} by KBr pellet technique. The optical transmittance and absorbance spectrum have been studied using a UV-Vis spectrophotometer in a wavelength region 190-900 nm. The presence of dopant in the crystal lattice have been analyzed by the instrument FEI QUANTA 200F energy dispersive X-ray microanalyser (EDAX). The TG-DTA analyses for the grown crystal have been carried out at nitrogen atmosphere by NETZSCH thermal analyzer. To confirm the SHG efficiency, the prepared Gd^{3+}:LHHCl single crystal have been subjected to Kurtz-Perry powder technique.

3. Results and discussion

3.1. Single crystal X-ray diffraction study

From the single crystal X-ray diffraction data, it is observed that the Gd^{3+}:LHHCl single crystal belongs to orthorhombic crystal system with the space group $P2_12_12_1$ which is recognized as noncentrosymmetric, thus satisfying the requirement for the SHG activity of the crystal. The cell parameters are shown in Table 1. It is compared with the parent material of L-Histidine hydrochloride crystal and the cell volume of Gd^{3+}:LHHCl single crystal is slightly increased from the previously reported [12].

Table 1. Single crystal data of Gd^{3+}:LHHCl crystal

Crystal	Gd^{3+}:LHHCl	
Formula weight	485.74 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.440 x 0.540 mm	
Crystal habit	Clear intense white COLUMNAR	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.8537(4) Å	α = 90°
	b = 8.9286(5) Å	β = 90°
	c = 15.2914(8) Å	γ = 90°
Volume	935.74(9) $Å^3$	
Z	2	
Density (calculated)	1.724 g/cm^3	
Absorption coefficient	0.306 mm^{-1}	
F(000)	506	

3.2. FT-IR spectral studies

In order to confirm the presence of various functional groups in Gd^{3+}: LHHCl, the grown crystal have been recorded and shown in Fig. 2. The observed peak and their corresponding assignments are listed in Table 2. The spectral bands are compared with known spectra of functional groups [13-15]. The FT-IR spectrum of Gd^{3+}: LHHCl shows a strong peak at 3486 cm^{-1} which is ascribed to O-H stretching vibrations of water molecule in the crystal. The broad absorption band observed at 2926 $cm^{-1}$is due to the presence of hydrogen bonding [16]. The C=O vibration of –COOH lies at 1628 cm^{-1} and O-H stretching of COOH appears at 1001 cm^{-1}. The CH_2 in plane bending mode appears at 1347 cm^{-1} and C-H plane bending is observed at 1170 cm^{-1} in FTIR spectrum. The torsional oscillation of NH_3^+ occurs at 532 cm^{-1}. The sharp absorption observed at 630 cm^{-1} is due to the ring deformation of the Gd^{3+}: LHHCl. In general, the peaks with frequencies in the range of 300-500 cm^{-1} belongs to rare earth metal bond. There is no significant absorption peaks observed between 1900 cm^{-1} to 3150 cm^{-1} in the Gd^{3+}: LHHCl spectrum. It shows the disappearance of carboxylic group. The FT-IR study confirms that the rare-earth metal Gd^{3+} coordinated to carboxylate group was observed in L-Histidine hydrochloride crystal.

Table 2. Functional groups of Gd^{3+}: LHHCl single crystal

Wavenumber (cm^{-1})	**Vibrational band assignments**
3486	O-H stretching
3357	N-H stretching
3172	C-H symmetric stretching
1628	C=O asymmetric stretch of –COO^-
1501	Symmetric C=C stretching and NH_2 bending
1423	Symmetric mode of COO^- and C-N stretching
1347	CH_2 bending
1170	C-H in plane bending
1099	C-O stretching of –COO^- group
1001	OH stretching of COOH
876	C-H out of plane bending
630	Ring deformation
532	Torsional NH oscillation of NH_3^+

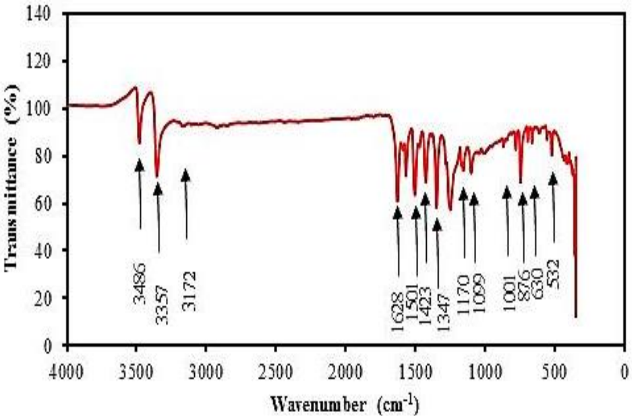

Fig. 2. FT-IR spectrum of Gd^{3+}: LHHCl single crystal

3.3. Ultraviolet-Visible spectroscopic studies

For optical applications, a grown crystal should be highly transparent in the visible region. The recorded absorbance and transmittance spectra are shown in Fig. 3 (a) and (b). From the absorption spectrum, the cut-off wavelength of the grown crystal is appeared at 250 nm. The doped crystal has lower UV cut-off wavelength compared with the pure L-Histidine hydrochloride crystal [12]. The absorption coefficient (α) of Gd^{3+}:LHHCl crystal was determined from the absorption spectrum.

The relation between the optical band gap (E_g), absorption coefficient (α) and energy (hν) of the incident photon using the Tauc equation [17, 18] is given by,

$$A h\nu = C(h\nu - E_g)^r \qquad (1)$$

where C the band tailing parameter, h is the Planck's constant, ν is the frequency of incident photon and r is the index number. The index number is 1/2 for direct allowed transition, 2 for indirect allowed transition, 3/2 for direct forbidden transition and 3 for indirect forbidden transition [19]. The transition number r value of grown crystal is equal to 0.5 (1/2) hence the direct optical band gap (Eg) was determined using the Tauc's relation and shown in Fig. 3 (c). The E_g of Gd^{3+}:LHHCl is estimated by extrapolating the linear region of the graph at $(\alpha h\nu)^2=0$ [20]. The calculated direct band gap (E_g) of Gd^{3+}:LHHCl is 5.1 eV which is in good agreement with the previously reported data [12]. The higher direct band gap of the grown crystal may have a few imperfections which might be the cause to act as best luminescent material.

The absorption coefficient (α) is related to the extinction coefficient (K) and is calculated by the following relation,

$$K = \alpha\lambda/4\pi \qquad (2)$$

where λ is the wavelength. Fig. 3(d) shows the variation of extinction coefficient (K) as a function of photon energy (hν). It is clear that the extinction coefficient depends on the photon energy [19]. Hence, the internal efficiency of the reported material can achieve the optimum laser threshold. Also, the grown crystal appears as a superior candidate to fabricate the optoelectronic devices.

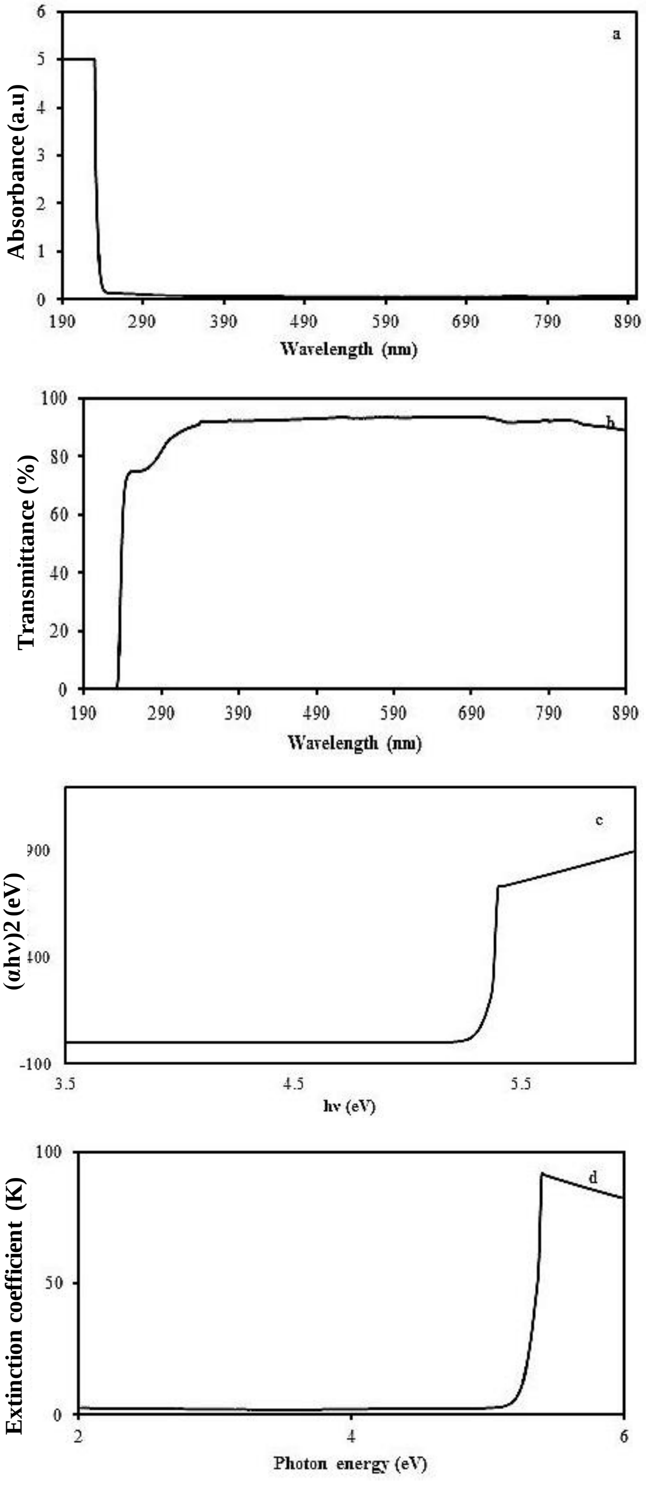

Fig. 3. UV-Vis optical (a) absorbance, (b) transmittance spectrum, (c) $(\alpha h\nu)^2$Vs hν (Tauc plot) and (d)Extinction coefficient (K) as a function of photon energy of Gd^{3+} ion doped LHHCl single crystals

3.4. Energy dispersive X-ray analysis

Energy dispersive X-ray analysis (EDAX) is a micro analytical technique used to obtaininformation regarding the elemental composition of the Gd^{3+}:LHHCl grown crystal. From the experimental data, the presence of Gd(III) intense peak is observedin the formation of Gd^{3+}: LHHCl single crystal as shown in the Fig. 4.

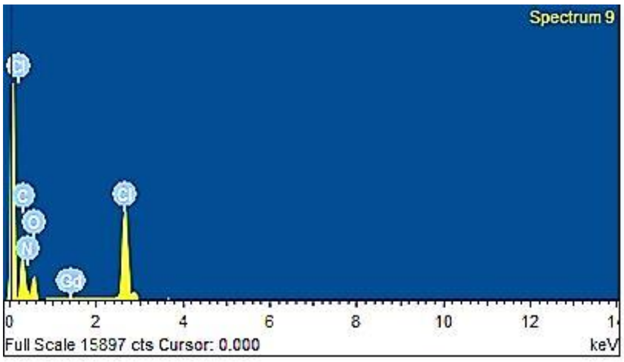

Fig. 4. EDAX spectrum of grown Gd^{3+}:LHHCl crystal

3.5. Thermal Analyses (TG-DTA)

To identify the thermal stability and melting point, thermo gravimetric-differential thermal analysis (TG-DTA) was recorded for the Gd^{3+}: LHHCl crystal. Initially, the sample with 4.217 mg weight was taken for TG-DTA measurement. The thermal curve was recorded in the temperature range between 28°C (RT) to 600 °C with the heating rate of 10 °C/min. The sample was recorded in nitrogen gas atmosphere and its characteristics curve is illustrated in Fig. 5. From the figure, first endothermic peak was appeared at 154.3 °C accompanied with a weight loss of 8.7%. The weight loss occurs due to the water moleculesevaporates from the Gd^{3+}: LHHCl crystalline molecule during the heating. The second endothermic peak occurred at 262.1 °C with higher weight loss due to the decomposition of Gd^{3+}: LHHCl crystal. The sharpness of endothermic peaks reveals the high crystallinity and high purity of the compound. Hence, the grown crystals confirms the good thermal stability compared with pure L-Histidine hydrochloride crystal [21].

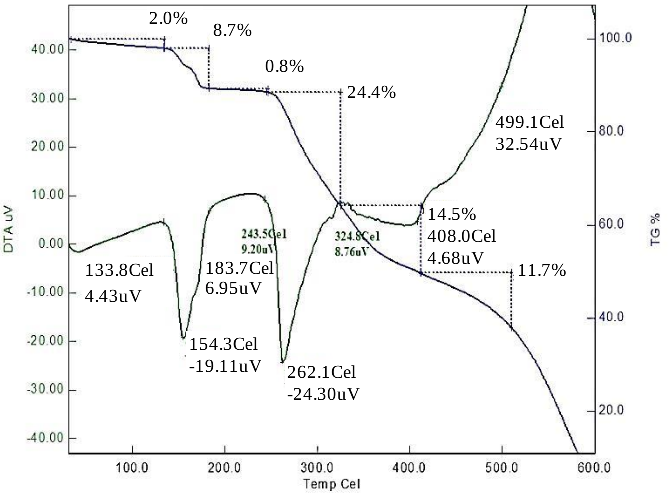

Fig. 5. TG-DTA of grown Gd^{3+}:LHHCl crystal

3.6. Second harmonic generation study

From the UV spectra, it is evident that theGd^{3+}:LHHCl crystal has cut-off wavelength at 250 nm which is more suitable for SHG or other applications in the blue region. Nonlinear optical property of Gd^{3+}:LHHCl crystal was confirmed by modified Kurtz-Perry powder technique [22]. The powder sample was densely packed in a needle-like glass capillary tube. The fundamental Nd: YAG laser beam of 1064 nm with pulse energy 1.2 mJ/s and pulse width of 10 ns and repetition rate of 10 Hz was used in the experiment and KDP is used as a reference for the comparison. A photo multiplier tube is used as a detector. The SHG property was confirmed by the emission of green radiationat 532 nm from Gd^{3+}: LHHCl material. The SHG efficiency for pure L-Histidine hydrochloride crystal is 3 times greater than that of KDP [12, 16]. In the present study rare-earth metal doped crystal (Gd^{3+}:LHHCl) shows 3.6 times greater than KDP. SHG efficiency of Gd^{3+}: LHHCl is 1.2 times than that of pure LHHCl.

4. Conclusion

Optically good quality single crystals ofgadolinium (III) ion doped L-Histidine hydrochloride have been grown at 30°C by slow evaporation solution growth technique. From the single crystal XRD data, the grown crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. The presence of functional group and molecular vibrations of grown crystal was identified by FT-IR spectrum. The absorption coefficient of the grown crystal was determined from the optical transmittance and the optical band gap (E_g) was calculated to be 5.1 eV. The presence of gadolinium ion in the crystalline lattice was confirmed by EDAX spectrum. The grown crystal was thermally stable up to154.3 °C and decomposed after the melting of the material. The NLO property was confirmed by SHG test which reveals that Gd^{3+}: LHHCl crystal has better efficiency compared to that of pure L-Histidine hydrochloride crystal which confirm the suitability of gadolinium (III) doped L-Histidine hydrochloride crystal for frequency conversion photonic device applications.

Acknowledgment

One of the author (N. Poongodi) grateful to the Department of Physics, Erode Sengunthar Engineering College for the financial support of the project. The authors wish to thank, Department of Physics, Bharathiar University, Coimbatore for single crystal XRD measurement and also grateful to Dr. P. K. Das, IISc, Bangalore for SHG measurement.

References

[1] T. Henningsen, N. B. Singh, R. H. Hopkins, R. Mazelsky, F. K. Hopkins, D. O. Frazier, O. P. Singh, Materials Letters **20**, 203 (1994).
[2] J. Madhavan, S. Aruna, P. C. Thomas, M. Vimalan, S. A. Rajasekar, P. Sagayaraj, Cryst. Res. Technol. **42**, 59 (2007).
[3] J. Madhavan, S. Aruna, K. Prabha, J. Packium Julius, Ginson P. Joseph, S. Selvakumar, P. Sagayaraj, J. Cryst. Growth **293**, 409 (2006).
[4] N. Vijayan, G. Bhagavannarayana, K. Nagarajan, V. Upadhyaya, Mater. Chem. Phys. **115**, 656 (2009).
[5] Yun Zhang, Hua Li, Bin Xi, Yunxia Che, Jimin Zheng, Mater. Chem. Phys. **108**, 192 (2008).
[6] A. Ben Ahmed, H. Feki, Y. Abid, H. Boughzala, C. Minot, Spectrochim. Acta part A **75**, 293 (2010).
[7] H. Fuess, D. Hohlwein, S. A. Mason, Acta Cryst. B **33**, 654 (1999).
[8] J. L. B. Faria, F. M. Almedia, O. Pilla, F. Rossi, J. M. Sasaki, F. E. A. Mela, J. Mendes Filho, P. T. C. Freire, J. Raman, Spectroscopy **35**, 242 (2004).
[9] K. Moovendaran, S. A. Martin BrittoDhas, S. Natarajan, Optik **124,** 3117 (2013).
[10] A. Ben Ahmed, H. Feki, Y. Abid, H. Boughzala, A. Mlayah, J. Mol. Struct. **888**, 180 (2008).
[11] P. Anandan, R. Jayavel, J. Cryst. Growth **322**, 69 (2011).
[12] S. Rajyalakshmi, K. Ramachandra Rao, B. Brahmaji, K. Samatha, T. K. Visweswara Rao, G. Bhagavannarayan, Optical Materials **54**, 74 (2016).
[13] L. J. Bellamy, The infrared spectra of complex molecules, 3rded. New York; Wiley; (1975).
[14] G. Herzberg, Infrared and Raman spectra of polyatomic molecules, 1sted. New York; Van Nostrand Reinhold; (1945).
[15] C. N. R. Rao, Chemical application of infrared spectroscopy, 2nded. New York; Academic Press; (1963).
[16] P. Anandan, R. Jayavel, T. Saravanan, G. Parthipan, C. Vedhi, R. Mohan Kumar, Opt. Mater. **34**, 1225 (2012).
[17] M. A. Kaid, A. Ashour, Appl. Surf. Sci. **253**, 3029 (2007).
[18] J. Tauc, Amorphous and liquid semiconductors, New York: Plenum Press: (1974).
[19] V. Krishnakumar, S. Sivakumar, R. Nagalakshmi, S. Bhuvaneswari, M. Rajaboopathi, Spectrochim. Acta A **71**, 480 (2008).
[20] P. D. Fochs, Proc. Phys. Society London, B **69**, 70 (1956).
[21] S. A. Martin BritoDhas, M. Suresh, G. Bhagavannarayana, S. Natarajan, J. Cryst. Growth **309**, 48 (2007).
[22] S. K. Kurtz, T. T. Perry, J. Appl. Phys. **39**, 3798 (1968).

---

*Corresponding author: dhanasekaranp1@gmail.com