Journal of King Saud University – Science 33 (2021) 101498

Contents lists available at ScienceDirect

Journal of King Saud University – Science

journal homepage: www.sciencedirect.com

Original article

Comprehensive studies on amino acid based organometallic L-threoninum cobalt (II) sulfate (LTCS) single crystal and its antibacterial and antifungal properties

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ARTICLE INFO

Article history:
Received 9 April 2021
Revised 6 May 2021
Accepted 29 May 2021
Available online 06 June 2021

Keywords:
Crystal growth
Optoelectronics Properties
Mechanical study
Antimicrobial activities

ABSTRACT

Highly transparent superior quality nonlinear single crystals of L-Threoninum Cobalt (II) Sulfate Heptahydrate were prepared by simple novel slow evaporation solution growth method. The space group, lattice parameters, crystal structure and crystalline nature of L-Threoninum Cobalt (II) Sulfate (LTCS) materials assessed through diffraction analysis (PXRD and SXRD). The optical behavior of LTCS crystals were checked via UV–Vis analysis and it confirms optical parameters often depend on photon energy with optical band gap E_g = 5.6 eV and LTCS material can be acceptable for optoelectronic devices. The hardness and work hardening coefficient of LTCS crystal were investigated using Vickers microhardness testing and the work hardening value 1.94 point out soft nature of the grown material. By use of Kurtz and Perry technique the nonlinear second harmonic generation (SHG) efficiency of prepared LTCS crystals was assessed. The LTCS material developed here is used to treat bacterial and fungal infections and is detected by an antimicrobial assay.

1. Introduction

Over the past few years, single crystals are extensively used for diverse applications because of their extremely high throughput in various fields. Apart from that, they provide high transparency, minimal defect, and high SHG efficiency (Masilamani et al., 2017). The periodicity of single crystals persists throughout the materials and is free from inner boundaries (Puhal Raj et al., 2013 & Rejnhardt and Daszkiewicz, 2021) and currently it plays a crucial role in everyday life because of their rising need for their potential applications. At present L-Threonine (amino acid) materials have shown superiority in several applications because it contains profusions of optically active atoms that demonstrate highly efficient SHG performance and are powerful material for in plenty of other applications (Elleuch et al., 2021 & Theerthagiri et al., 2021). For this reason that amino acid-based single crystal forms the foundation for science and Technology. Amino acid molecule exhibits double ions anion and cation in the same molecule (Allen Moses et al., 2019). This happens when the amino group got protonated and the carboxylic acid group is deprotonated at the same time (Hemalatha et al., 2019 and Duraimurugan et al., 2021). Such double ions are called Zwitterions which enhancing the nonlinear optical (NLO) response (Yoneda et al., 2020). L threonine is an active amino acid which is used to treat many different types of nervous system disorders as well as a processing additive and a substrate for the biosynthesis of several other chemicals. Cobalt II sulphate is a cobalt salt that is used in the manufacturing of pigments and a number of other cobalt salts. In the context of the above concern, the present investigation describes physico-chemical properties of LTCS crystal.

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.jksus.2021.101498
1018-3647/

2. Materials and methods

2.1. Materials and crystal growth

By using familiar slow evaporation solution growth technique with highly purified chemicals purchased from Sigma-Aldrich we have been grown a good quality LTCS nonlinear single crystal. For the growth of LTCS crystal, a sufficient measure of L-Threonine and Cobalt (II) Sulfate heptahydrate was dissolved in highly purified laboratory water with the aid of magnetic stirrer at 40 °C for over almost 3–4 h. Even after the solution as filtered for the removal of contaminants and retained unabated evaporation state for the growth of LTCS crystals, and between 25 and 30 days good quality L-Threonine Cobalt (II) Sulfate heptahydrate crystal were gathered as depicted in Fig. 1 below.

2.2. Characterization techniques

With the help of Bruker Kappa APEXII X-ray technique, the unit cell parameters were determined for the grown LTCS crystals. XPERT-PRO diffractometer was used to determine the PXRD studies with Cu Kα radiation having wavelength λ = 1.5406 Å was scanned over a range from 10°– 80° at the scan rate of 2^0/min, for analyzing grown crystal's crystalline nature. The UV–Vis spectrum of grown LTCS sample has been measured over diverse range of 200–800 nm by UV-1700 Series Spectrophotometer (Kalyanaraman et al., 2015). The mechanical behavior of grown crystal was studied with the help of HMV-2 T microhardness tester. Kurtz and Perry technique were applied to determine the SHG efficiency of LTCS crystal (Siva Shankar et al., 2009). With the help of the controls such as Amikacin (for antibacterial) and Nystain (for antifungal) the antimicrobial activities of LTCS was ensured by disk diffusion method.

3. Results and discussion

3.1. Powder X-ray diffraction analysis (PXRD)

LTCS crystal's PXRD assessment was conducted by grinding the defect-free LTCS crystal into small particles and it was analyzed with varying 2θ values' ranging from 10^0-80^0 for the scan rate of 2 degree per minute is illustrated in Fig. 2.

The sharp and distinct peaks observed at precise 2θ angle confirms high crystalline nature and structural phase purity of the LTCS material (Vivekanandhan et al., 2018 & Araújo et al., 2019).

3.2. Single crystal X-ray diffraction analysis (SXRD)

SXRD method gives the information about unit cell parameters and space group of the LTCS crystal (Abila et al., 2020). The

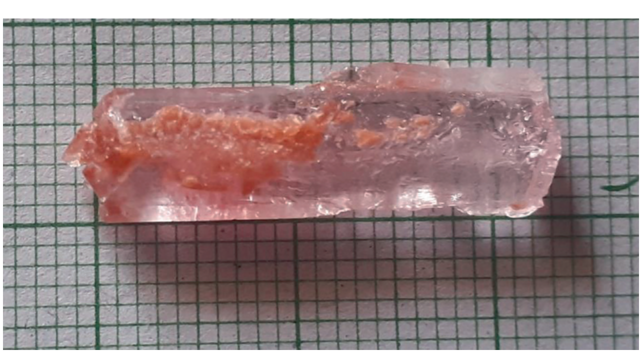

Fig. 1. Photograph of LTCS single crystal.

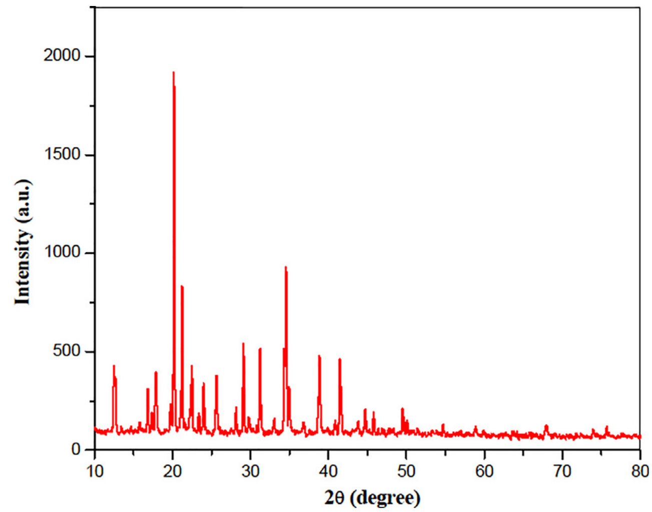

Fig. 2. Powder XRD pattern of LTCS crystal.

obtained data depicts that the grown crystal belonging towards the class of orthorhombic system by means of non-centrosymmetric space group $P2_12_12_1$, is an elementary condition for SHG application (Suresh and Sagadevan, 2014). The analysis shows that the developed single crystal has a = 5.56 Å, b = 8.19 Å, c = 13.94 Å, α = β = γ = 90^0 and cell volume obtained was 634 $Å^3$ and this values are concord with the reported literature (Allen Moses et al., 2019).

3.3. UV–Visible spectral analysis

Much knowledge about optical transitions is given by optical constants such as the absorption coefficient, optical extinction coefficient, optical refractive index, and optical (Subhashini et al, 2019; Karuppasamy et al., 2020).

Fig. 3(a) in LTCS crystal shows a wide transparency window from 250 to 800 nm and no absorbance within that range. The titular material is active with 83% transmittance indicating that the LTCS crystal possess greater optical transparency and the prepared crystals were suitable for NLO applications (Hanumantharao and Kalainathan, 2012a, 2012b). By using Tauc's relationship (Dillip et al., 2012) 'α' (optical absorption coefficient) and band gap can be determined using the following expressions (Allen et al., 2019). For LTCS crystal n = 1/2 indicated the direct bandgap nature of the material, and this direct bandgap materials used to make optical devices such as LEDs and semiconductor lasers etc.

$$\alpha = \frac{2.303}{t}\log\frac{1}{T} \tag{1}$$

$$\alpha h\nu = A(h\nu - E_g)^n \tag{2}$$

Fig. 3(b) exposed the plot between $(\alpha h\nu)^2$ and hν, it provides the value E_g (band gap) = 5.6 eV for LTCS crystal and this wider E_g reveals LTCS material is suitable for designing and assembly of optoelectronic devices (Chennakrishnan et al., 2017). Reflectance (R) and Refractive indexes (n) of LTCS crystal were carried out by means of the following equation and are plotted versus hν as exposed in Fig. 3 (c & d).

$$R = 1 \pm \frac{\sqrt{1 - exp(-\alpha t) + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \tag{3}$$

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{4}$$

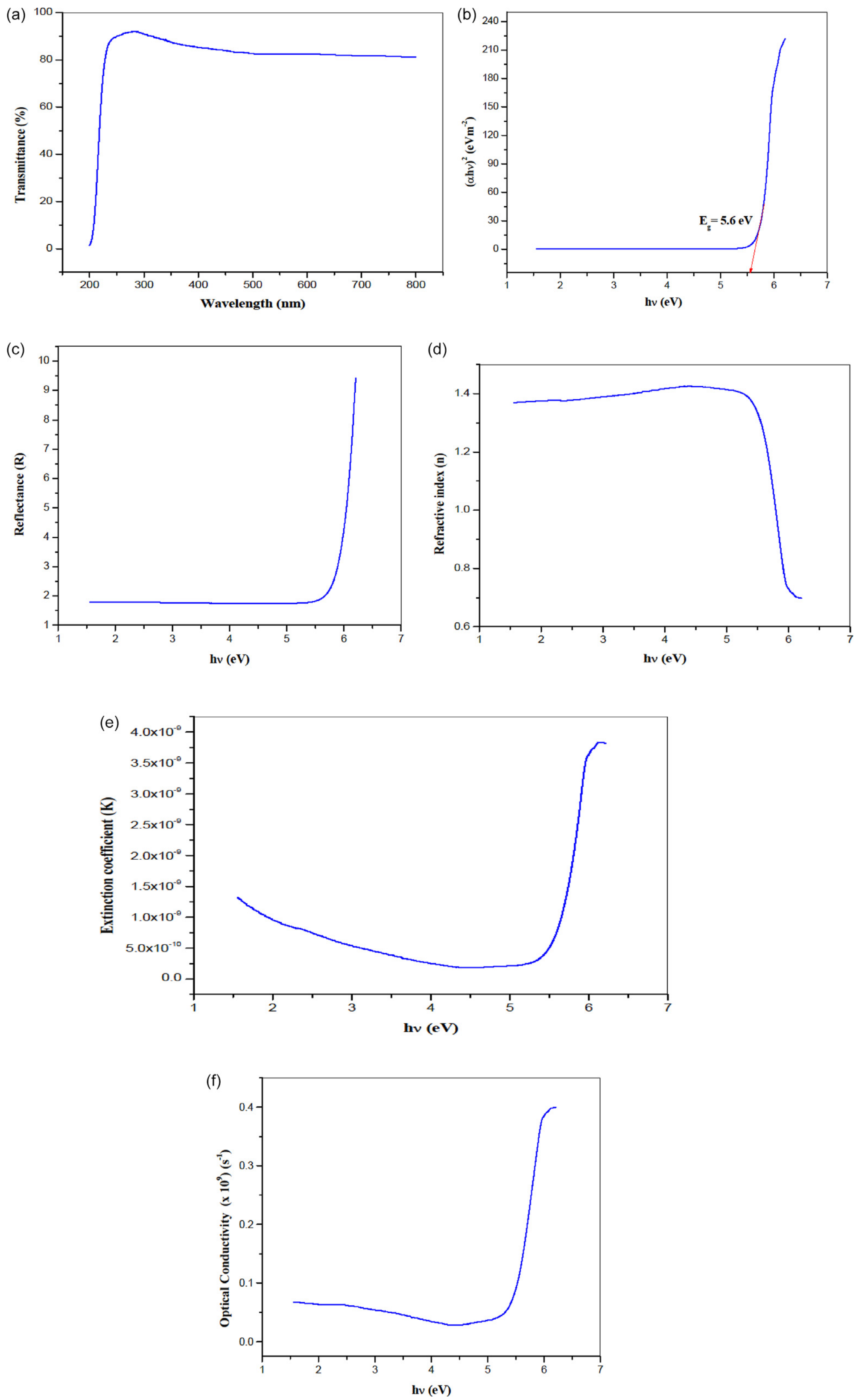

Fig. 3. (a) Transmission spectra of LTCS crystal, (b) Plot of $(\alpha h\nu)^2$ versus ($h\nu$) of LTCS crystal, (c) Photon energy versus R, (d) Photon energy versus n, (e) Extinction Coefficient with $h\nu$ of LTCS crystal, (f) Optical conductivity with $h\nu$ of LTCS crystal.

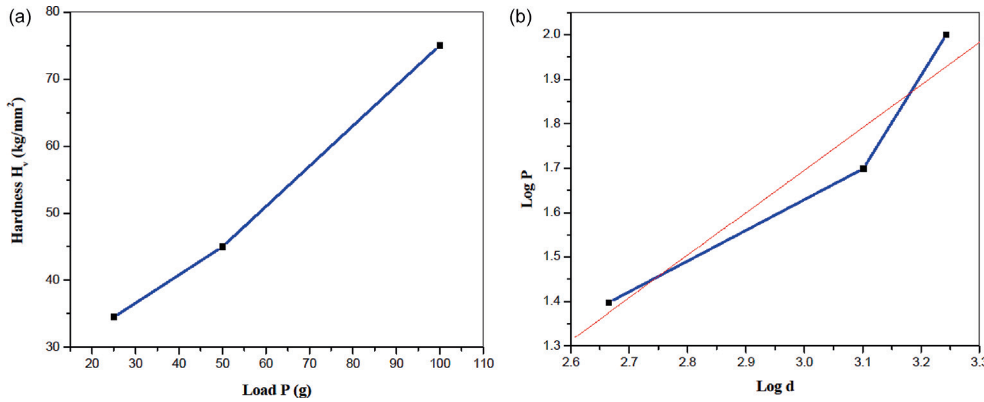

Fig. 4. (a) Hardness versus load P of LTCS crystal, (b) Log P versus Log d of LTCS crystal.

In Fig. 3(c and d) it is understood that these optical parameters suchlike R and n depend on hν shows the LTCS materials are suitable for manufacturing optoelectronic devices. The extinction coefficient (K) indicates the absorptivity of the grown material and it can be calculated by the following equation:

$$K = \frac{\lambda\alpha}{4\pi} \quad (5)$$

Where all symbols have their own significance.

Fig. 3(e) shows the material is highly translucent in the lower energy region because the small value of extinction coefficient, while a larger value indicates higher degrees of opacity. For use as optical material, a low extinction coefficient is essential.

$$\sigma = \frac{\alpha nc}{4\pi} \quad (6)$$

Using the above equation, we can easily find out the optical conductivity of the prepared LTCS crystal.

The variation of Optical conductivity with respect to hν for LTCS crystal is exposed in Fig. 3(f). It displays that, how when optical conductivity drops significantly, hν is increased and is essential for optoelectronic applications. (Subhashini et al., 2019).

3.4. Mechanical studies

The mechanical property of the prepared material was measured by Vickers micro-hardness test (Surekha et al., 2014). Herein the indentation mark of the LTCS crystal was measured by varying the load (25 g, 50 g, and 100 g) for indentation time 10 s. H_v (hardness number) can be calculated using the following relation

$$H_v = 1.8544P/d^2 \quad (7)$$

Where all the symbols have their own significance.

It is observed from the Fig. 4(a) that H_v of the LTCS crystal increases up to a load of 100 g enunciate the RISE (reverse indentation size effect) displayed by the crystal and it is useful for any application (Sangwal 2000).

The type of the crystal was determined by means of following Meyer's law.

$$P = Ad^n \quad (8)$$

$$LogP = \log A + n\log d \quad (9)$$

The Meyer index 'n' can be determined from the slop of a graph drawn for log d versus log P.

The work hardening value 1.94 is estimated from Fig. 4(b) As Onitsch explained the value of 'n' for harder materials is between 1and 1.6, over 1.6 the substance shall be known as soft material (Onitsch 1956). Anyhow, the LTCS material is beneficial for NLO applications because this material is a softer category (Hanumantharao and Kalainathan, 2012).

Table 1
Growth inhibition zones of LTCS crystal.

Microorganisms		Control (mm)	LTCS (mm)
Bacteria	*Escherichia coli*	20	13
	Klebsiella pneumoniae	19	15
	Staphylococcus aureus	21	10
Fungi	*Candida albicans*	15	14
	Candida parapsilosis	15	10
	Aspergillus flavus	12	9

3.5. Nonlinear optical studies

In order to test the nonlinear SHG efficiency, the titular compound was illuminated with Q-switched Nd: YAG laser (1064 nm) and the green light of wavelength 532 nm was emitted by LTCS crystal was measured and the result obtained is compared with KDP (Bhuvaneswari and Nalini, 2018; Kurtz and Perry, 1968). This confirms that the SHG output of grown LTCS crystal was 1.32 times that of standard KDP crystal (MartinBritto et al., 2008; UmaDevi et al., 2008). It is clear from the observation that the presence of Co^+ ions which enhances the effect of titular crystal. Here the greater SHG performance of the grown sample ensures it can be beneficial for different NLO applications (Chandrasekaran et al., 2012).

3.6. Antimicrobial activity

The microbial activities of LTCS material were demonstrated using the disc diffusion process. To understand the bacterial activity, antibacterial susceptibility testing is performed for LTCS material using microorganisms namely *Escherichia coli, Klebsiella pneumoniae,* and *Staphylococcus aureus* and the results are presented in Table 1. The result obtained shows that LTCS material resists the growth of specified above most susceptible microorganisms, nevertheless, on a comparative the result indicated that LTCS material showed a substantial resistivity against *Klebsiella pneumonia* than the other two microorganisms as shown in Fig. 5 (a, b, & c). The inhibitory activity on *Escherichia coli* of LTCS material is greater than that of macrocyclic dinuclear Zn(II) complex (Kou et al., 2020). Because of the result obtained, the developed material may be suitable for the treatment of various diseases caused by the above mentioned microorganisms (Aneeba et al., 2020; Priya et al., 2020).

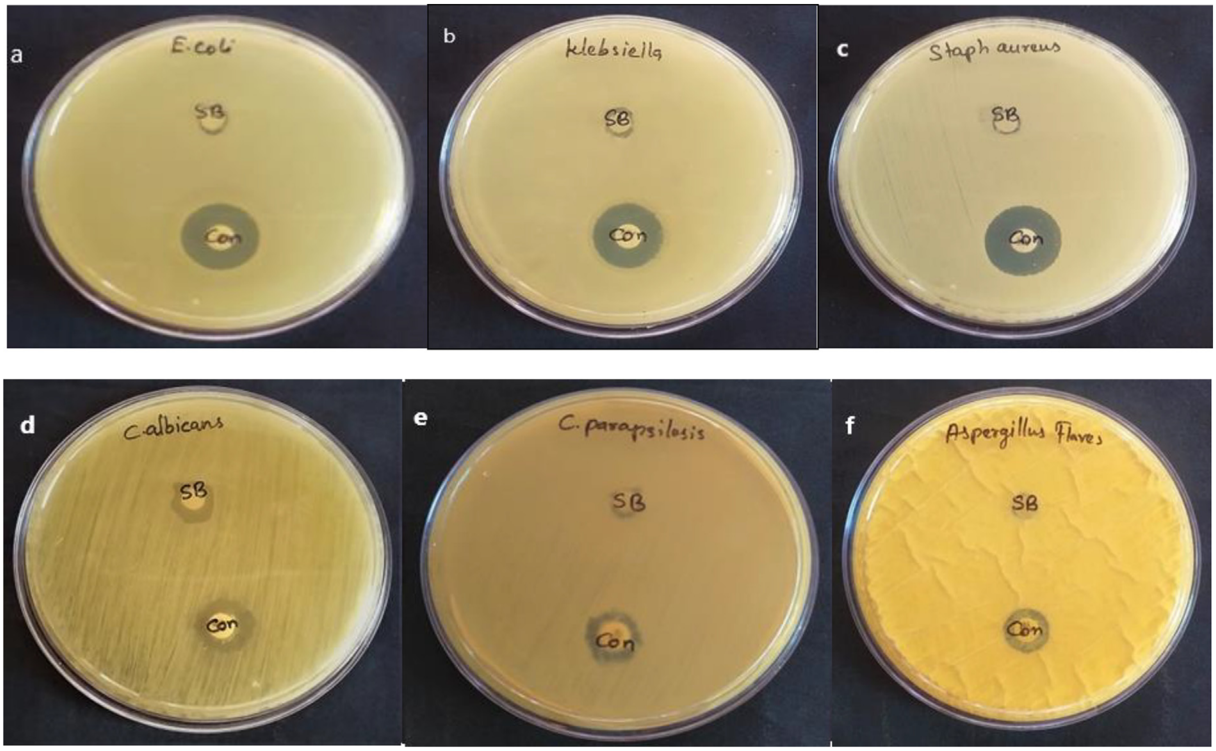

Fig. 5. Antibacterial activity of LTCS crystal for three bacterial pathogens (a) *Escherichia coli* (b) *Klebsiella pneumoniae* (c) *Staphylococcus aureus,* Antifungal activity of LTCS crystal for three fungal pathogens (d) *Candida albicans* (e) *Candida parapsilosis* (f) *Aspergillus flavus.*

To access the antifungal activity, LTCS material were screened against three different test organisms namely *Candida albicans, Candida parapsilosis* and *Aspergillus flavus* as shown in Fig. 5 (d, e & f) and the obtained results are presented in Table 1 .The result suggest that among three fungi, LTCS highly inhibited the activity of *Candida albicans* (15 mm) than other two fungi. However, according to the results obtained, LTCS sample makes resistance to the most prevalent opportunistic fungal pathogens. In the context of above concern the grown material can be used to treat various diseases caused by the above-mentioned three pathogenic fungi (Aneeba et al., 2020 & Abid et al., 2019).

4. Conclusions

The LTCS crystals were effectively grown using slow evaporation method. SXRD data reveals that the LTCS crystal having orthorhombic arrangement with non-centrosymmetric space group $P2_12_12_1$.The crystalline natures of LTCS crystal were confirmed by PXRD analysis. The UV–Vis spectrum clearly shows the compound is active in the entire visible region with 83% transmittance and E_g was found to be 5.6 eV. Micro-hardness testing reveals the softer nature of the grown LTCS crystal. The nonlinear SHG efficiency of LTCS crystal was 1.32 times that of the KDP crystal. Antimicrobial assay confirms LTCS material resist the growth of some microorganisms. The results of the above-mentioned studies indicate that, the sample produced can be used to plenty of applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The writers wish to express their gratitude to SAIF IIT, Chennai, Ayya NadarJanakiammal College, Sivakasi, for the facilities given for different analyses. The authors extend their appreciation to Taif University for funding current work by Taif University Researchers Supporting Project number (TURSP-2020/295), Taif University, Taif, Saudi Arabia.

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