



Physico-chemical properties, SHG and THG studies of an semiorganic NLO material L-glutamic acid nickel chloride

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Abstract Semiorganic nonlinear optical L-Glutamic acid Nickel Chloride (LGANC) single crystals were harvested using the slow evaporation solution growth method at room temperature. The LGANC crystal belong to the orthorhombic system and space group was analysed by powder XRD Techniques. Functional group present in the sample were identified by FTIR spectral analysis. The crystal were characterized by UV–Vis–NIR Transmission spectrum in the range of 200–1100 nm. Photoluminescence spectral study revealed the electron excitation in the grown crystal. SHG conversion efficiency was investigated, and it reveals 1.23 times greater than KDP reference material. The thermal stability of LGANC was determined using TGA and DTA. Surface morphology of the grown crystal was examined by using SEM analysis. To demonstrate the third-order susceptibility of the produced crystal, Z-scan technique were used. It is important that the title material has a variety of excellent physicochemical and nonlinear optical characteristics, which assists it in gaining recognition as a prospective candidate for nonlinear optical device applications.

Keywords LAGNC · Nonlinear optics · Thermal stability · Microhardness · Photoluminescence · Z-scan

Introduction

High performance crystals are most important for commercial and industrial applications. Recently, organic and inorganic non linear materials are revealing their good properties and focusing on optoelectric applications and optical device fabrications [1–3]. In general, the organic crystals exhibited poor thermal behavior, mechanical properties and absorption edge is in blue region, and their cut of wave length exceeding 450 nm, because of these, its not possible to grow in the huge size[4–6]. To overcome these drawbacks and improve the opto electrical, NLO, mechanical properties by using different metal/inorganic ‘d’ block elements.

Most of the advantages of novel crystal types in technological applications are due to the ease with which semiorganic crystals grow in bulk in all three dimensions, making the manufacturing process of devices easier[7–10]. As a result of semi-organic crystals high non-linearity, high laser damage resistance, low angular sensitivity, and superior mechanical hardness, organic materials strong NLO characteristics and chemical flexibility combine with inorganic materials’ physical sturdiness and excellent transmittance[11–14].

Recently, researchers have been particularly interested in amino acid-based complex crystals owing to their adaptability for mixing with a variety of inorganic compounds and their proclivity for crystallisation in crystal systems suitable for nonlinear optical applications. Additionally, the combination of organic compounds with high NLO efficiency with inorganic materials with desirable physical characteristics has been a focus of study. The current article discusses the development and characterisation of a single crystal of L-Glutamic acid Nickel chloride using the slow evaporation solution growth method. We calculated the nucleation parameters and a variety of other factors.

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Materials and methods

Materials

Commercially available high purity 99.8% analytical reagent chemicals L-Glutamic acid and 99.9% purity of nickel chloride were purchased from Merck and Sigma-Aldrich.

Synthesis and growth of LGANC

The LGANC crystal was grown by an equal molar ratio (1:1) of L-Glutamic acid and nickel chloride. The short procedure is shown in Table 1. In double distilled water at 40 °C, the estimated quantity of LGA was first soluble. The solution of nickel chloride was then added to the parental solution slowly and sonicated well. After 6 h, it turned into a homogeneous solution. The solution was filtered four or five times using Whatmann filter paper to eliminate any undesirable contaminants. A dust-free location with an aluminium foil sheet was used to store the filtered parental solution. The slow evaporation solution technique was used to generate the LGANC crystal. The recrystallisation process is used to improve the high purity of the crystal. After 45 days, a clear excellent grade LGANC crystal with a size of $8 \times 9 \times 2 \text{ mm}^3$ was obtained. The reaction scheme of the title compound, L-Glutamic acid nickel chloride as shown in Fig. 1 and the photo image of the grown crystal is as shown in Fig. 2.

Characterization

An ENRAF NONIUS CAD4 diffractometer and $\text{MoK}\alpha$ radiation ($=0.71073 \text{ \AA}$) were used to perform a single crystal X-ray diffraction experiment, scanning from 10 to

Table 1 Crystallization of LGANC

1	Solvent	Double distilled water
2	Temperature	45 °C
3	Period of crystal grown	45
4	Size	$8 \times 9 \times 2 \text{ mm}^3$
5	Rate of growth	0.77 mm/day

Fig. 1 Diagram showing the LGANC crystal reaction

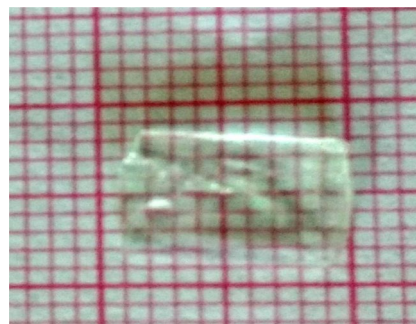
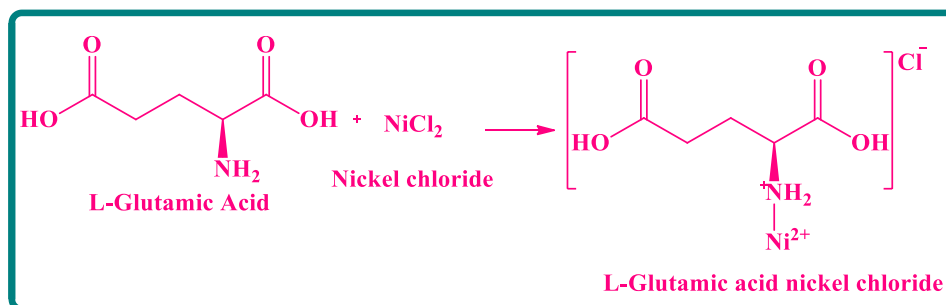


Fig. 2 An image of a grown LGANC crystal

80° at a scan rate of 1°/min. The formed crystal powder X-ray diffraction was studied with a BRUCKER, Germany (model D8 Advance) X-ray diffractometer utilising $\text{CuK}\alpha$ (wavelength = 1.5405 Å) radiation. With the use of an Alpha Bruker and a KBr pellet, the FTIR spectrum was captured. Dupont 951 thermogravimetric analyzer was used to test the crystal thermal stability by performing TGA analysis. Second harmonic generation (SHG) experiments on Kurtz-perry powder were carried out using a spectra-physics quanta-ray pro lab 170 Nd:YAG laser with a first harmonic input of 1064 nm and a pulse width of 10 ns at a repetition rate of 10 Hz. To examine the crystal surface morphology, researchers used a field emission scanning electron microscope (FESEM; Hitachi S4800; Japan).

Results and discussion

Single crystal X-ray diffraction

According to the results, the XRD analysis of a single crystal revealed that the LGANC crystal belongs to an orthorhombic crystal system with the non-centro symmetric space group P_{212121} . The calculated lattice parameter values are enumerated in Table 2 and are in agreement with the reported pure LGA crystal [15].

Table 2 Single crystal XRD crystallographic data of LGANC

Unit cell parameter	Pure L-glutamic acid (LGA) crystal [15]	LGANC crystal
a (Å)	$a=5.17$	$a=5.15$
b (Å)	$b=6.95$	$b=7.76$
c (Å)	$c=17.35$	$c=13.67$
$\alpha=\beta=\gamma$	90°	90°
Volume (Å ³)	623.411	547.23
Crystal system	Orthorhombic	Orthorhombic

Powder X-ray diffraction study

Powder XRD measurements confirmed the crystalline nature of the generated LGANC crystal powder sample. Figure 3 depicts the powder XRD patterns that were discovered throughout the testing process. LGANC high crystalline character may be seen in the well-defined Bragg's peaks at certain 2θ angles (10–80°). Observing the Bragg's peak at specified 2θ angles verifies the crystals purity and clarity. The planes observed in powder XRD patterns were indexed using the standard powder X software. It is observed that the diffraction peak of each evident plane is distinct and sharp which admits the crystalline nature of grown crystals. The reports of plane wave dynamical theory of X-ray diffraction suggest that the material with less full width half maxima (FWHM) exhibit good crystalline nature.

FTIR studies

Figure 4 shows the assignment peak and their absorbed frequencies of LGANC crystals. The stretching vibration

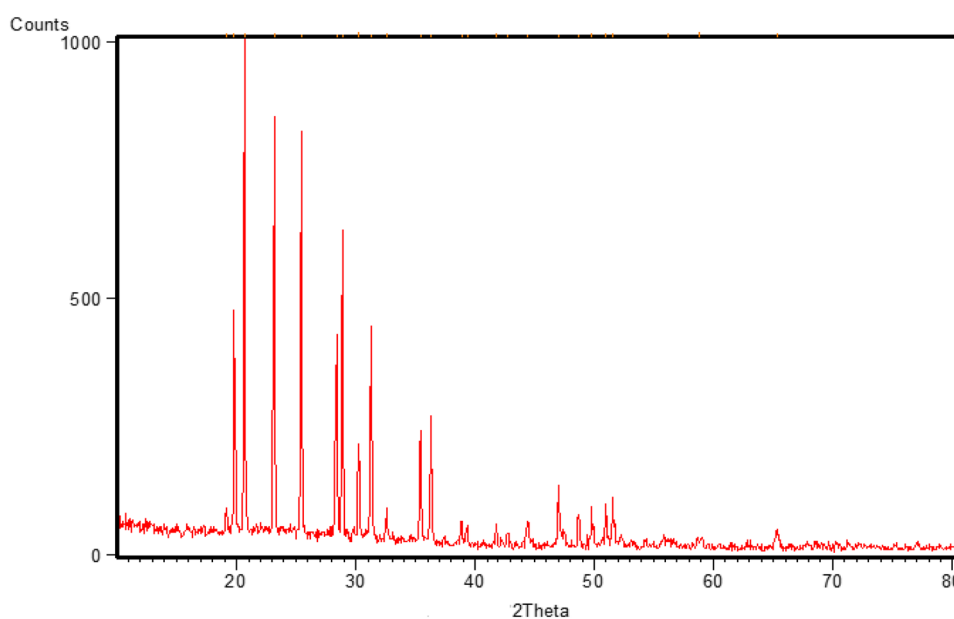
of the NH_3^+ group was found to be responsible for the peak value of 3137 cm^{-1} . The wide peak at 1725 cm^{-1} was attributed to COO^- stretching vibration, as was the corresponding broad peak. The presence of strong peak observed at 1680 cm^{-1} corresponded to C=O group, while 1404 cm^{-1} was due to stretching of the OH deformation [16]. The high frequency peak observed at 1508 cm^{-1} was attributed to NH_3^+ symmetric vibration and the other sharp peak at 999 cm^{-1} due to CH_2 rocking. The 863 cm^{-1} was corresponding to presence of C-C-N symmetric vibration. There was a peak at 533 cm^{-1} that looked like an organometallic chee linkage. This could be because the sample had the Ni^{2+} ion in it [16].

Optical transmission studies

Figure 5 shows the UV–Vis–NIR transmittance spectrum for a grown crystal. The crystal shows good transmittance in the visible region and a maximum cut-off wavelength at 232 nm. A wide transparent window is observed at 232 nm, and there is no absorption is noticeable between 232 and 1100 nm region which indicates that the crystal has good optical transmission with lesser defects. Growing samples with improved optical characteristics allows opto electronic applications to take advantage of those improvements [17]. We can figure out how much band gap energy exists at this wavelength by plugging in the formula:

$$E_g = hc/\lambda_c(\text{eV}) \quad (1)$$

where h , c , e are constants and λ is the wavelength. The band gap energy of LGANC was estimated to be 5.3 eV. The

Fig. 3 Powder XRD pattern on grown LGANC crystal

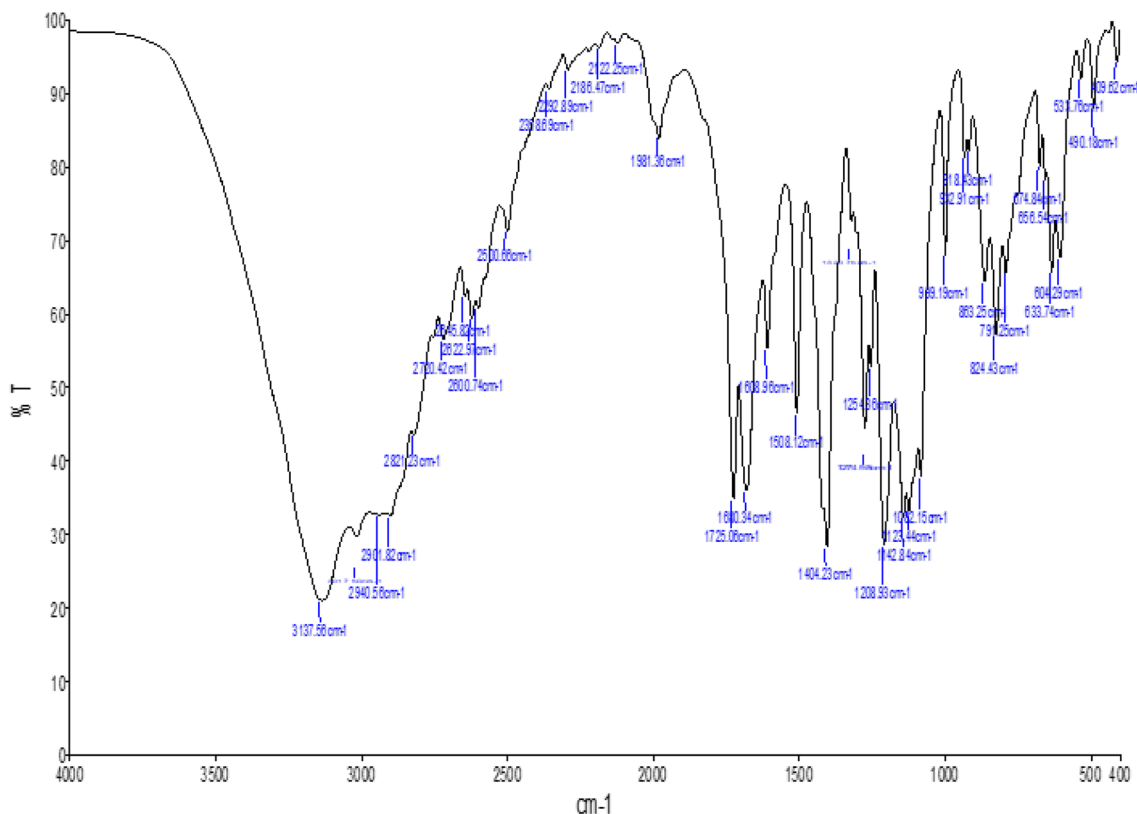


Fig. 4 FTIR spectrum of LGANC

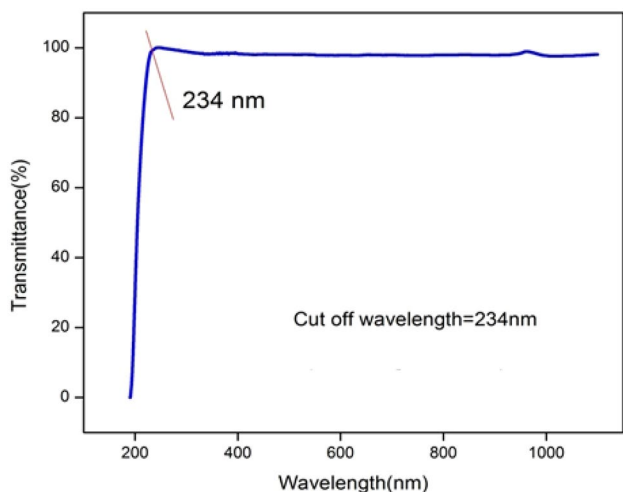


Fig. 5 UV-Vis-NIR spectrum of grown LGANC crystal

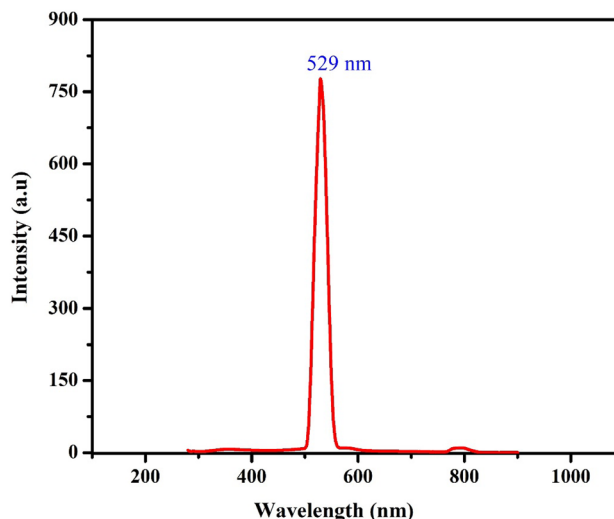


Fig. 6 LGANC crystal PL emission spectrum

broad transmittance window and low absorption of LGANC wide band gap indicate that the material is suited for NLO applications [18].

Photoluminescence study

Figure 6 shows the PL emission spectrum of a grown LGANC crystal, recorded in the range from 0 to 1000 nm. According to the results, the crystal emits strong light fluorescence with an emission peak of 529 nm. Because of the

crystal anionic and cationic composition, additional peaks appeared [19].

SHG efficiency studies

Powder SHG test offers the possibility of assessing the nonlinearity of new materials. The input power was set to 0.701 J and the output power was determined to be 10.72 mJ, which was compared to a typical potassium Dihydrogen phosphate (KDP output of 8.91 mJ). LGANC crystal powder SHG efficiency was determined to be 1.23 times that of normal KDP. The produced crystals are shown to be a good material for optical device applications [20].

Thermal studies

Figure 7 shows the TGA/DTA analysis of the LGANC crystal. The first weight loss was observed at 180 °C and major weight loss was obtained at 260 °C. These weight loss are coincidences with the DTA curve. To be exact, the material melts around 240 °C and there is no phase change until the substance melts completely. It shows that the LGANC crystal has greater thermal stability than previously reported [21]. The TGA/DTA analyses indicate that the generated crystal is suitable for photonic and optoelectronic device applications.

SEM analysis

SEM is used to obtain information about surface topography and composition. The presence of some visible inclusions deposited on the surface of the crystals was seen in the micrograph of the crystal, which was due to Ni atoms. Figure 8 shows the SEM images of the grown LGANC crystal. SEM examination was performed on crystals that were produced

with well-structured planes and a smooth surface [22, 23]. SEM examination reveals a perfectly smooth surface devoid of fractures, gaps, valleys, and dislocation network, confirming the generated crystal perfection. On the crystal surface, some microcrystalline are observed due to the presence of nickel.

Z-scan studies

Third-order nonlinear optical characteristics, such as the nonlinear absorption coefficient (β), nonlinear refractive index (n_2) and third-order nonlinear susceptibility ($\chi^{(3)}$) are easily and generally helpful for the investigation using the Z-scan technique [24]. To utilise the Nd:YAG laser beam of wavelength 532 nm as the source and to concentrate the focal length of the lens via the convex lens, the focal length of the lens was set to 103 mm. Open and closed apertures are used to calculate intensity dependent nonlinear optical characterizations such as n_2 , β , and $\chi^{(3)}$ [25]. The measurement of the aperture when closed and open and plotted normalized transmittance verses Z-position as shown in Figs. 9 and 10. In the closed aperture pattern of the LGANC crystal has a peak followed valley which gives an indicated negative nonlinearity index and it is self-defocusing. Following equation, it was calculated that the refractive index of the generated crystal was nonlinear.

$$n_2 = \frac{\Delta\phi}{Kt_{\text{eff}}I_0} \tag{2}$$

As irradiance increases at focus, I_0 (the on-axis irradiance) decreases, and K is equal to $2\pi/\lambda$. Also, λ is the wavelength of the laser beam, with K equal to $2\pi/\lambda$. Lastly, t_{eff} is the effective sample thickness, with $\Delta\phi$ equal to the phase shift. It evokes the saturable absorption, the higher intensity of the open aperture Z-scan transmission near the focus. Nonlinear absorption β was calculated from Z-scan data by [26].

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0t_{\text{eff}}} \tag{3}$$

where the highest Z-scan value, ΔT , is found. An experimental value of n_2 and β are used to compute the real and imaginary portions of the third-order nonlinear susceptibility $\chi^{(3)}$.

$$\text{Re}\chi^{(3)} = \frac{10^{-4}(\epsilon_0 C^2 n_0^2 n_2)}{\pi} \tag{4}$$

$$\text{Im}\chi^{(3)} = \frac{10^{-2}(\epsilon_0 C^2 n_0^2 n_2 \lambda \beta)}{4\pi^2} \tag{5}$$

when we take into consideration the fact that C is the light velocity on the vacuum surface, the permittivity of a vacuum

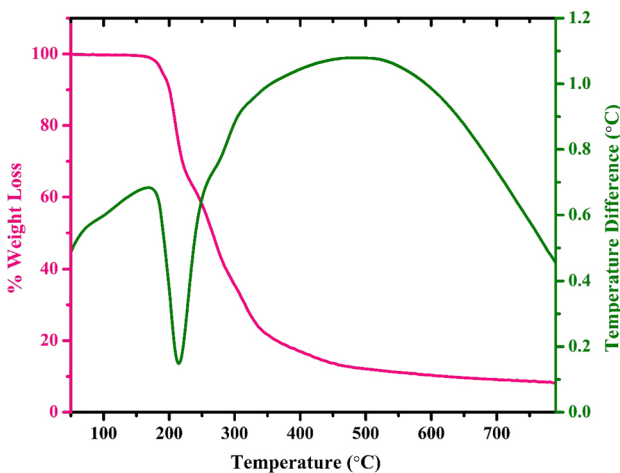


Fig. 7 TG/DTA diagram of LGANC crystal

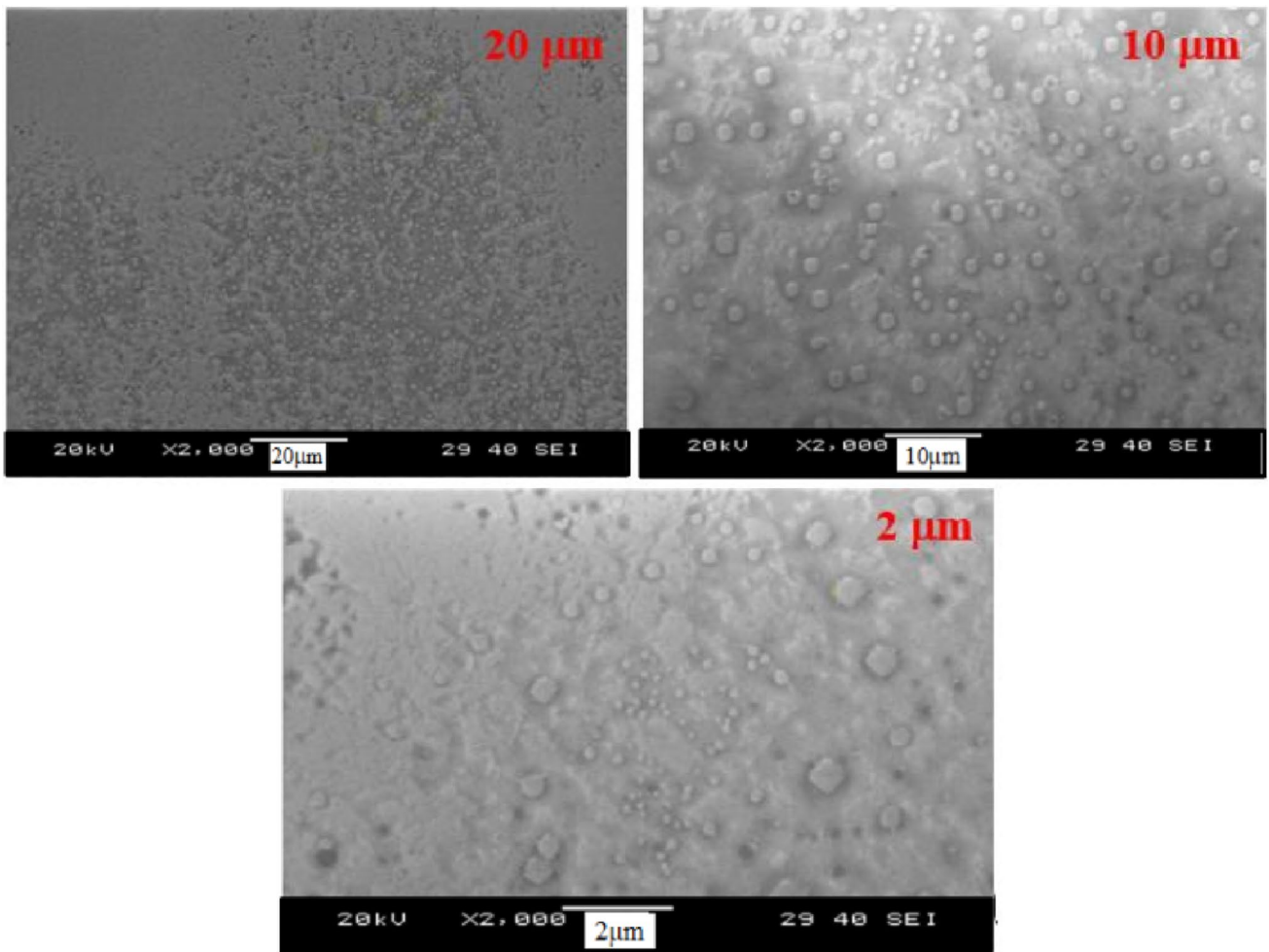


Fig. 8 SEM images of LGANC crystal

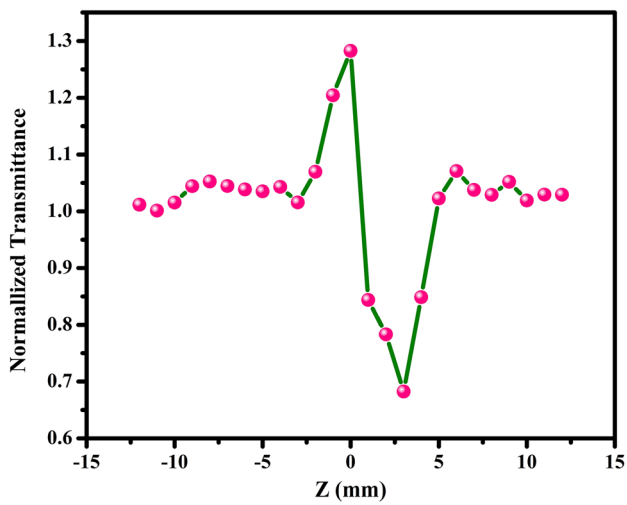


Fig. 9 Closed aperture curve of LGANC

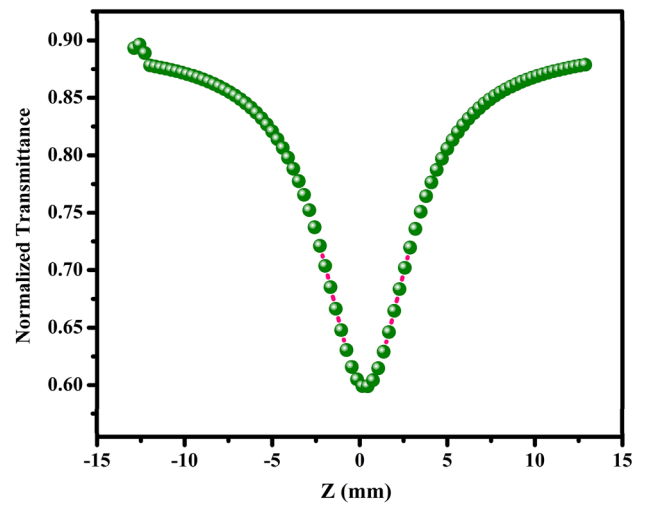


Fig. 10 Open aperture curve of LGANC

Table 3 Presents the results of third-order NLO characteristics for LGANC crystals

Parameters	Measured LGANC crystal values
Laser beam wavelength (λ)	532 nm
Linear absorption coefficient (α)	1.2066 m ⁻¹
Nonlinear refractive index (n_2)	2.543 × 10 ⁻¹⁰ cm ² W ⁻¹
Nonlinear absorption coefficient (β)	0.0209 × 10 ⁻⁴ cm W ⁻¹
Real susceptibility [Re(χ^3)]	1.117 × 10 ⁻⁸ esu
Imaginary susceptibility [Im(χ^3)]	1.984 × 10 ⁻⁸ esu
Absolute susceptibility (χ^3)	2.329 × 10 ⁻⁸ esu

is given by the formula ϵ_0 , and the linear refractive index of the utilised sample is n_0 and the wavelength of the laser beam is λ , we arrive at the conclusion that there was an exact calculation to get the exact value of $\chi^{(3)}$ using the following relationship [27].

$$|\chi^{(3)}| = \sqrt{(\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2} \quad (6)$$

The Nonlinear optical properties for the estimated third-order have been compiled into a Table. 3.

Conclusion

In summary, a high-quality non-linear optical semi-organic single crystal was successfully obtained at room temperature using a slow evaporation method. Single crystal X-ray diffraction and powder XRD methods were used to determine the unit cell characteristics, crystal system, and crystal-line nature. FTIR research was used to validate the various functional groups in the LGANC crystal. The LGANC crystal's UV–Vis–NIR cut-off wavelength was determined to be 234 nm, and its optical band gap to be 5.3 eV. Electron excitation was detected in the formed LGANC crystal using photoluminescence spectroscopy. SHG efficiency analysis demonstrated that the LGANC crystal efficiency was 1.23 times greater than the KDP efficiency. TG/DTA revealed that the melting point of grown crystal is 240 °C. SEM morphology revealed the uniform surface of the synthesized LGANC crystal. The Z-scan method displays the LGANC crystal own self-defocusing effect. Hence, the title crystal is a more potential compound for fabrication of NLO and Opto-electronic devices.

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