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Review Article

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Studies on Growth and Characterization of Bis-Glycinium Oxalate (BGLO) Crystals

GP Sankar Ganesh[1*], U Sankar[2] and P Selvarajan[3]

[1]*Department of Physics, S.T.Hindu College, India*
[2]*Department of Physics, K.G.S. Arts & Science College, India*
[3]*Department of Physics, Aditanar College of Arts and Science, India*

ABSTRACT

Single crystals of bis-glycinium oxalate (BGLO) were grown from the aqueous solution by slow evaporation growth technique by taking glycine and oxalic acid in the molar ratio 2:1. The lattice parameters of the grown crystal was confirmed by single crystal XRD analysis and crystalline nature was identified by powder X-ray diffraction method. Solubility of the material was gravimetrically analyzed. The presence of functional groups in the grown crystal was identified from FTIR spectral studies. Optical behaviour of the title compound was analyzed by using UV-visible spectrophotometer. The mechanical strength of the grown crystal was found from Vickers microhardness measurement. The thermal behaviour of the grown crystals has been investigated by TG/DTA analysis and the impedance analysis was performed for the sample to understand the electrical properties. SHG test reveals that the grown crystal is a centrosymmetric and third-order NLO material.

Keywords: Amino acid complex; Single crystal; Solution growth; Characterization; XRD; Spectroscopy; impedance; TG/DTA

INTRODUCTION

In recent years, the search of nonlinear optical materials is increased due to their importance in the field of telecommunication, optical computing, optical data storage and optical information processing [1-4]. Advanced laser based imaging, optical communication and data storage systems require improved nonlinear optical materials [5-7]. Organic crystals can exhibit higher nonlinear optical efficiencies than those of inorganic materials due to large optical susceptibilities, high optical threshold for laser power and low frequency dispersion [8,9].Organic materials are often formed by weak Van der Walls and hydrogen bonds and hence possess a high degree of delocalization. In the field of nonlinear optical growth, amino acids are playing a vital role [10]. Amino acids and their complexes belong to a family of organic and semi-organic materials that have been considered for photonic and NLO applications [11]. The significance of amino acids in NLO applications is due to the fact that most of the amino acids have chiral symmetry, efficient NLO property and crystallize in non-centrosymmentric space groups [12-15]. When an organic material is mixed with an amino acid, NLO property is increased due to the zwitterionic nature and high transparency range [16, 17]. Hence in this work, oxalic acid has been mixed with glycine to synthesize bis-glycinium oxalate salt. Single crystals of the synthesized salt were grown by slow evaporation technique and the grown crystals were characterized by various studies.

Synthesis, growth and solubility of the sample

Bis-glycinium oxalate (BGLO) sample was prepared by dissolving analar grade glycine and oxalic acid in stoichiometric ratio 2:1 in double distilled water. The solubility of BGLO in double distilled water was determined by gravimetrical method [18] as a function of temperature in the range 30° - 50° C. The figure 1 shows the solubility curve. From the graph it is observed that the solubility increases with the temperature. In accordance with the solubility curve, the synthesized powder of BGLO was dissolved thoroughly in double distilled water at 30 ^oC to form saturated solution. The solution was kept in undisturbed conditions and maintained at room temperature. Transparent seed crystals were obtained after ten days. The big sized crystals were obtained using seed immersion technique after 20 days. The harvested single crystals of the title compound are shown in figure 2 and the grown crystals are observed to be colourless and transparent.

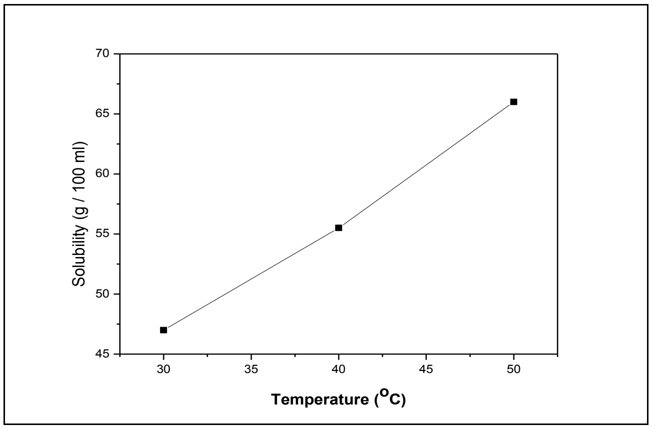

Figure 1: Solubility curve of BGLO sample

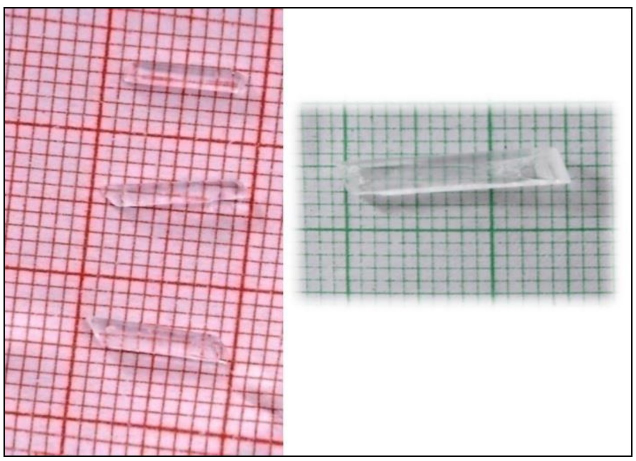

Figure 2: Harvested single crystals of BGLO

Studies of the crystals

Structural properties by XRD studies:

From the single crystal X-ray diffraction analysis, it is found that the BGLO crystal crystallizes in monoclinic system with a space group $P2_{1/n}$ and unit cell dimensions are a=4.941 (3) Å, b=9.945(2) Å , c=10.904 (2) Å, α = 90.00^o , β = 98.42^o, γ = 90.00^o. The volume of the system is V=530.25 Å^3. The observed lattice parameters for BGLO crystal are found to be in good agreement with reported values [19]. The crushed fine powder of BGLO is subjected to powder X-ray diffraction analysis by using XPERT-PRO diffractometer with CuK_α radiation (λ=1.5406 Å).The radiation in the powder form was scanned in the reflection mode in the 2θ range 10°-80° at the rate of 1°/s. Figure 3 depicts the powder XRD pattern of the BGLO crystal. From the powder pattern, the crystalline perfection is confirmed by the presence of sharp diffraction peaks. Powder XRD data for BGLO sample are given in the

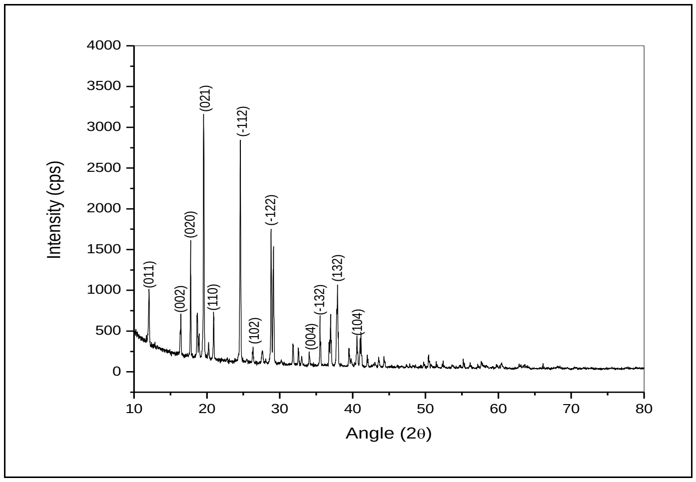

Figure 3: Powder XRD pattern of BGLO crystal

Table 1: Powder XRD data for BGLO crystal

Peak No	2θ (degrees)	d-spacing (Å)	h k l	Rel. Int. [%]
1	12.077	7.33	11	21.42
2	16.437	5.39	2	16.51
3	17.77	4.99	20	38.46
4	19.545	4.54	21	100
5	20.927	4.24	110	18.43
6	24.596	3.61	-112	90.99
7	26.334	3.38	102	6.53
8	28.799	3.1	-122	55.41
9	34.026	2.63	4	5.6
10	35.519	2.53	-132	19.78
11	37.933	2.37	132	34.12
12	41.142	2.19	104	14.27

FTIR analysis

The infrared spectral analysis is effectively used to understand the chemical bonding and it provides information about molecular structure of the synthesized compound. Each and every one chemical compounds have their own typical IR spectrum [20].The FTIR Spectrum of the title material was recorded in the wave number range 400-4000 cm^{-1} by KBr pellet technique with a Perkin-Elemer RXI Spectrometer and is shown in the Figure 4. The intense sharp peak at 1718cm^{-1} is due to the C=O stretching of COOH. The CH_2 bends are observed at 1412 cm^{-1}. The NH_3^+ absorption, the characteristic of amino acids, occurring at higher wave number 3126 cm^{-1}. The NH_2 group of glycine is protonated by COOH group giving rise to NH_3^+ and COO- group during the formation of the compound. and COO^- wagging vibration occurs at 660 cm^{-1}.The absorption band occurs at 878 cm^{-1} is corresponding to CN stretching mode.

UV-vis-NIR transmittance studies

A transmission spectrum is very important for NLO materials. In this study, a BGLO crystal of thickness 2 mm has been used. UV-visible transmittance spectrum of the crystal was recorded using Perkin- Elmer – Lambda 35 UV-vis spectrophotometer in the range of 200-1100 nm. The recorded optical spectrum is shown in figure 5. From the spectrum it is seen that the crystal has a lower cut-off wavelength of 295 nm and it is the essential parameter for frequency doubling process using diode and solid state laser [21]. The value of E_g of the BGLO crystal comes out to be 4.203 eV from the graph. It is observed that there is no significant absorption in the visible and infrared spectral regions and it indicates the better optical quality of BGLO crystal.

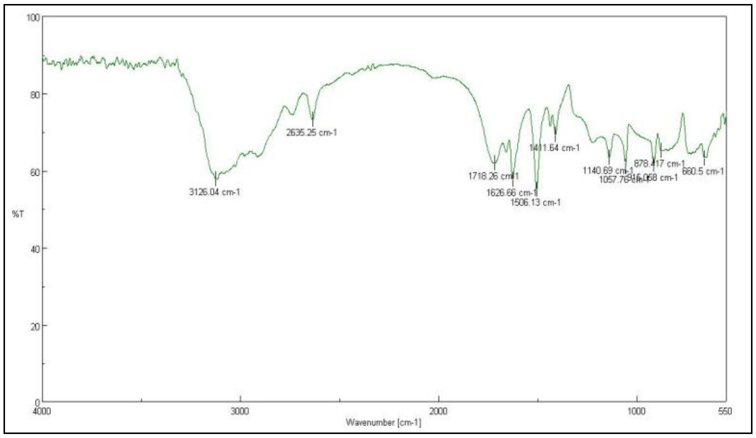

Figure 4: FTIR spectrum of BGLO crystal

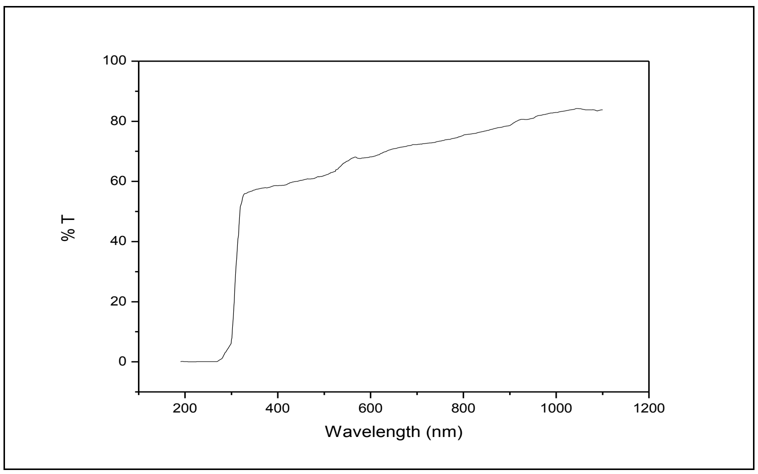

Figure 5: Transmission spectrum of BGLO crystal

Vickers microhardness analysis

Microhardness analysis of the BGLO was carried out using Vickers microhardness tester attached to a microscope. In this work, the intender is kept at right angles to the crystal plane for 10 s in all cases. Microhardness is the property of a material to exhibit its capacity to resist indentation. Vickers microhardness number was determined using $H_v = 1.8544\ P/d^2$ where P is the applied load and d is the diagonal length of the indentation impression [22]. The relation between the hardness number (Hv) and load (P) for BGLO crystal is shown in figure 6. The hardness number was found to increase with the increase in load. Mayer's law relates load and size of indentation as $P=a\ d^n$ where a and n are constants. The plot of log d versus log P is shown in figure 7. From the plot, the Mayer's index or work hardening coefficient (n) is determined. The value of n is found to 2.5629. According to Onitsch, n should be below 1.6 for hard materials and above 1.6 for softer ones [23]. Hence, BGLO crystal is a soft material.

Thermal analysis

The thermal analysis was carried out by TG/DTA studies using Perkin Elmer thermal analyzer from 36° C to 700° C at a heating rate 10° C/min in the nitrogen gas atmosphere to determine the thermal stability of the title compound. The recorded TG/DTA curves are shown in figure 8. A weight of 19.160 mg in powder form of the compound was used for the above study. The TG trace appears nearly straight up to the temperature 82.13° C and upto this temperature the sample is thermally stable. There are three endothermic peaks at 82.13 ^oC, 109.21 ^oC and 147.58 ^oC in the DTA curve and these are due to liberation of water molecules from the sample. The major weight loss occurs from 170° C to 250° C and it may be due to decomposition point of the title compound. Finally 8.865 mg left as a residue.

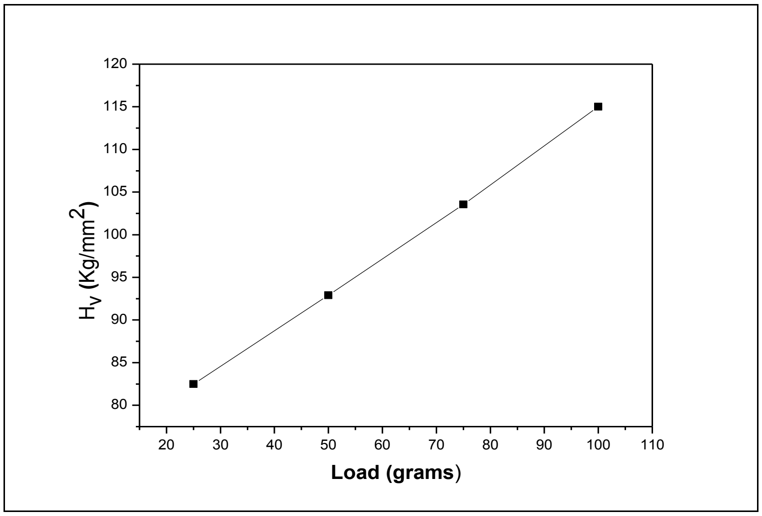

Figure 6: Plot of H_v versus load for BGLO crystal

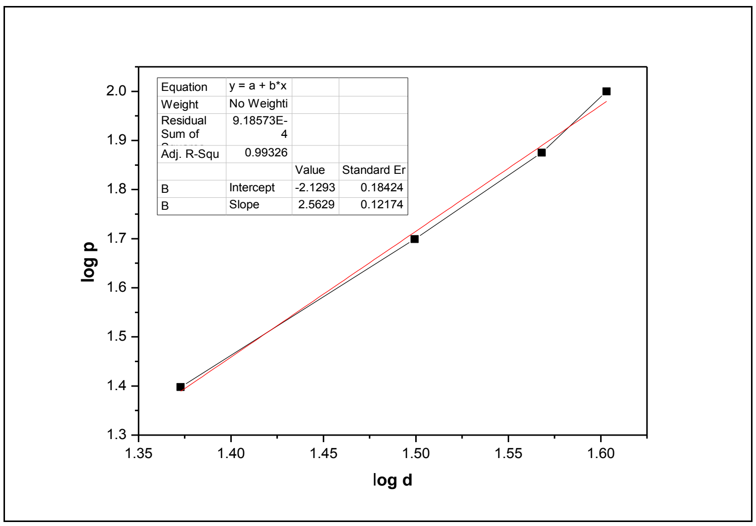

Figure 7: Plot of Log P versus log d for BGLO crystal

Impedance analysis

Impedance spectroscopy is a powerful technique for the characterization of electrical behaviour of the crystal. The electrical parameter such as impedance is a complex quantity and it has real part and imaginary part of impedance. Figure 9 shows the variation of the real part of impedance (Z') with frequency at various temperatures. It is observed that the magnitude of Z' decreases with the increase in both frequency as well as temperature, indicating an increase in AC conductivity with the rise in temperature and frequency. The Z' values for all temperatures merge above 10 kHz. This may be due to the release of space charges as a result of reduction in the barrier properties of material with the rise in temperature and may be a responsible factor for the enhancement of AC conductivity of the material with temperature at higher frequencies. Further, at low frequencies the Z' values decrease with rise in temperature show negative temperature coefficient of resistance (NTCR) type behaviour like that of semiconductors.

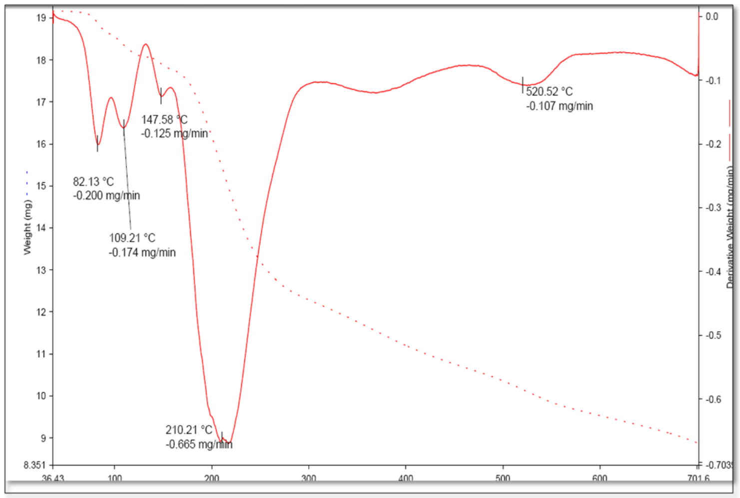

Figure 8: TG/DTA curves of BGLO crystal

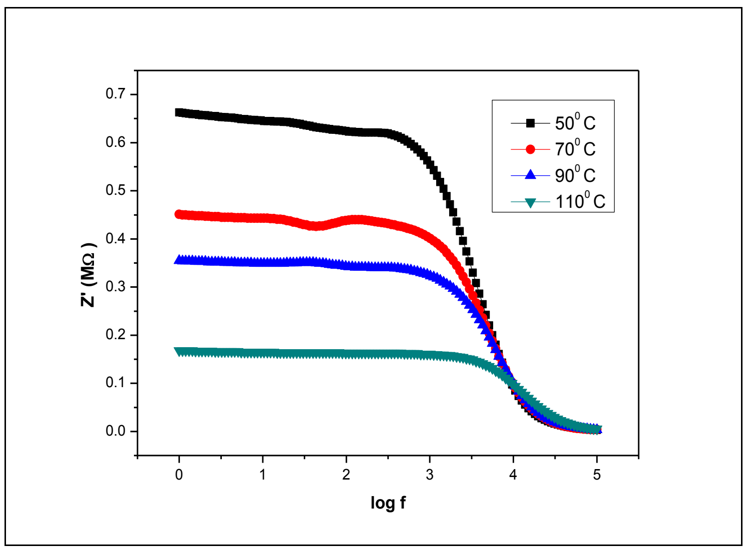

Figure 9: Variation of real part of impedance (Z') with frequency at different temperatures for BGLO crystal

Figure10 shows the variation of imaginary part of impedance ($Z^{'}$) with frequency at different temperatures. This plot is suitable for evaluation of the relaxation frequency of most resistive contribution. The relaxation frequency peak shifts to higher frequencies with increasing temperature, indicating the relaxation in the system. The relaxation frequency of BGLO crystal at 50 ^{o}C is found to be 3100 Hz and it increases with increase of temperature. The relaxation frequency can also be obtained from the plots of semicircles from the Nyquist plot. The peak broadening on increasing temperature, suggests the presence of temperature dependent relaxation processes in the compound [24]. The relaxation process may be due to the presence of immobile species at low temperature and defects at higher temperature.

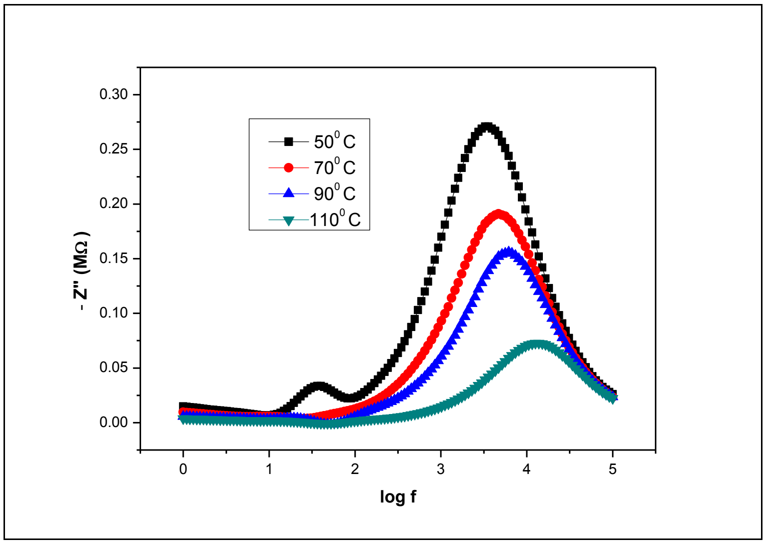

Figure 10: Plots of imaginary part of impedance versus frequency for BGLO crystal

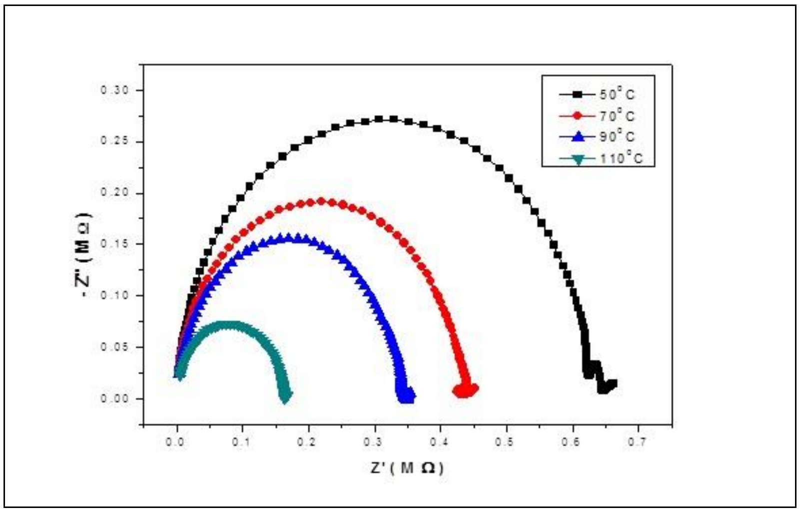

Figure 11: Nyquist plot between Z' and Z" for BGLO crystal

Figure11 shows a set of impedance data taken over a wide frequency range (1 Hz – 100 kHz) at different temperatures as a Nyquist diagram. The semicircles for the different temperatures could be traced, indicating the increase in conductivity of the sample. All these curves start at almost same value and do not coincide with origin. It can also be observed that the peak maxima shifts to higher values of frequency with the increase in temperature. The existence of grain boundary conduction of the sample has been observed. The value of bulk resistance (R_b) and grain boundary resistance (R_g) at different temperatures has been obtained from the intercept of the semicircular arc on the real axis ($Z^{'}$) and also the dc conductivity of the sample at different temperatures were found. The value of bulk resistance (R_b) and grain boundary resistance (R_{gb}) of BGLO crystal at different temperatures are given in the table 2.

Table 2: Values of bulk resistance, grain boundary resistance and DC conductivity for BGLO crystal

Temperature	Bulk resistance (MΩ)	Grain boundary resistance (MΩ)	DC conductivity x 10^{-7} (ohm-m)$^{-1}$
50 °C	0.62	0.33	442.4
70 °C	0.44	0.22	663.6
90 °C	0.34	0.17	858.8
110 °C	0.16	0.08	1825

SHG test

Second order nonlinear optical (NLO) activity has been tested by Kurtz-Perry powder technique [25]. The grown crystal of BGLO was ground into fine powder and subjected to second harmonic generation (SHG) test. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was allowed to strike the sample cell normally. It is noticed from the measurement that BGLO crystalline sample does not provide SHG and there is no green light emitted from the sample and it gives the conclusion that the grown crystal has zero second-order susceptibility coefficient. Hence, it is concluded that BGLO crystal is a centrosymmetric crystal and it shall have a third order NLO activity.

CONCLUSION

Single crystals of BGLO can be successfully grown by slow evaporation method. The grown crystals were characterized by X-ray diffraction analysis which shows that the bis-glycinium oxalate (BGLO) crystal belongs to the monoclinic system. The powder X-ray diffraction analysis shows that the crystal has high crystalline structure. The FT-IR spectroscopic analysis confirms the molecular structure of the compound. The UV-vis-NIR transmittance spectrum shows a good optical transmittance and the lower cut off at 295 nm. The mechanical property of the grown crystal shows that the crystal belongs to the soft mechanical category. The mechanical strength of the grown crystal has been analyzed and work hardening coefficient of the sample has been obtained. The real part and imaginary part of impedance were measured as a function of frequency and temperature for the sample and bulk resistance, grain boundary resistance and DC conductivity values were estimated. SHG test indicates that BGLO crystal is a third-order NLO material.

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