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CHARACTERIZATION OF GAMMA GLYCINE CRYSTALS GROWN USING RUBIDIUM CHLORIDE AS AN ADDITIVE (GGRC)

T. Gladys Vimala*, E. Bena Jothy* & P. Selvarajan**
* Department of Physics, Women's Christian College, Nagercoil, Tamilnadu
** Department of Physics, Aditanar College of Arts and Science, Tiruchendur, Tamilnadu

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Abstract:
Gamma glycine crystals using rubidium chloride as an additive (GGRC) were grown at room temperature (31 ^{o}C). The saturated aqueous solution was prepared by dissolving glycine and rubidium chloride in 3:1 molar ratio and single crystals of gamma glycine were grown in a period of four weeks by slow evaporation method. The grown crystals of GGRC were characterized by single crystal XRD analysis, UV-visible transmittance studies, dielectric studies, mechanical studies, LDT studies, The Second Harmonic Generation (SHG) efficiency of the sample was measured using a Nd:YAG laser. The results from the different studies show that gamma glycine crystal is an excellent nonlinear optical (NLO) material.

Key Words: Gamma Glycine, Solution Growth, Single Crystal, Characterization, X-Ray Diffraction, NLO & Vickers Hardness

1. Introduction:

Amino acids are used to prepare the complexes of organic and semiorganic NLO materials [1]. Glycine is the simplest amino acid that crystallizes in six different polymorphic forms viz. α, β, γ, δ, ε and β' - forms. α-glycine is optically inactive and it has been reported that **α-glycine** combines with H_2SO_4, $CaCl_2$, $CaNO_3$, $BaCl_2$ and AgNO3 to form useful NLO crystals [2-7]. Among the six forms of glycine, gamma glycine (γ-glycine) exhibits strong piezoelectric and NLO effects [8, 9]. Gamma glycine crystallizes in a non-centrosymmetric space group $P3_2$ and it has the excellent NLO properties [10, 11]. The crystal structure of gamma glycine was solved and it was published in the literature in 1958 [12]. Recently, growth and various studies of γ-glycine crystals have been reported by many authors and it is observed that γ-glycine crystals have been grown using additives such as potassium chloride, sodium chloride, lithium chloride, potassium bromide, ammonium chloride etc [13-16]. In this work, α–glycine is converted into γ-glycine using rubidium chloride as an additive. The aim of this paper is to report the growth of γ-glycine crystals by slow evaporation method and to discuss the results obtained from the various studies.

2. Growth of Gamma Glycine Crystals:

AR grade chemicals such as glycine and rubidium chloride were purchased and used without any further purification. Glycine and rubidium chloride were taken in the molar ratio of 3:1 and the calculated amounts of the chemicals were dissolved in double distilled water, stirred well using a magnetic stirrer and the saturated solution was prepared. The solution was filtered using Whatmann filter paper and was taken in a growth vessel covered with a perforated paper. This arrangement was kept in a vibration-free place in the laboratory for slow evaporation. Transparent seed crystals appeared in the growth vessel after a period of 10 days. Seed immersion solution growth technique was used to grow big-sized crystals of gamma glycine. The harvested crystals were non-hygroscopic, highly transparent and free from inclusions. The ability of the nucleation of gamma glycine in presence of rubidium chloride is probably due to a modification of molecular arrangements resulting from the columbic interactions between rubidium chloride and glycine molecules. The grown crystal of gamma glycine using rubidium chloride as an additive (GGRC) is shown in the figure 1. Here let us call this sample as GGRC crystal.

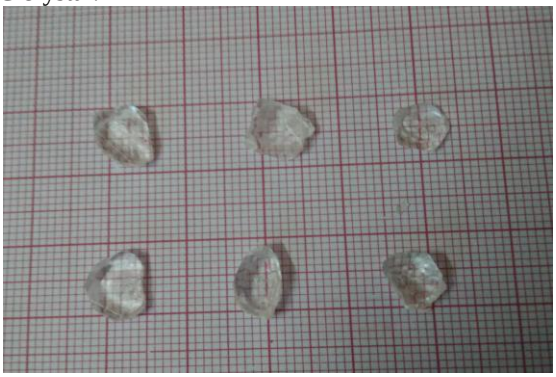


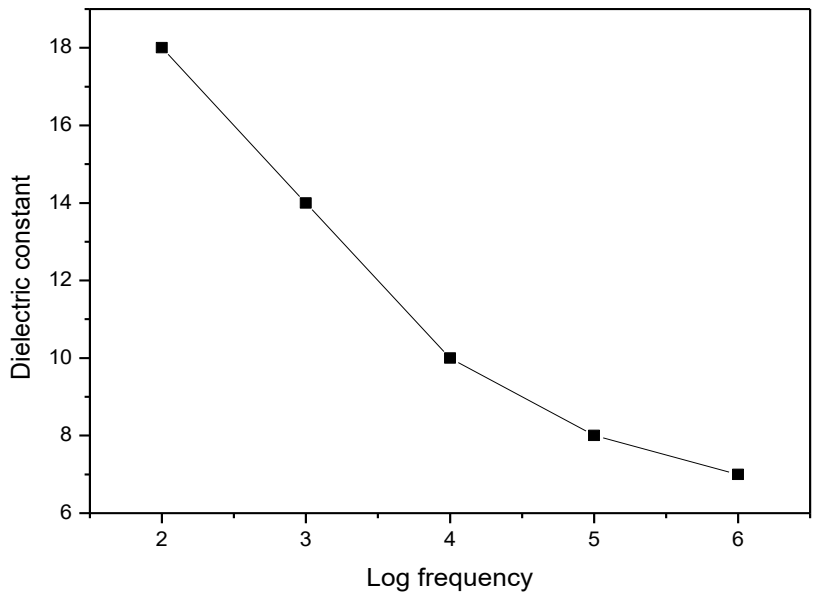
Figure 1: The grown crystal of gamma glycine using rubidium chloride as an additive (GGRC)

3. Instrumental Methods:

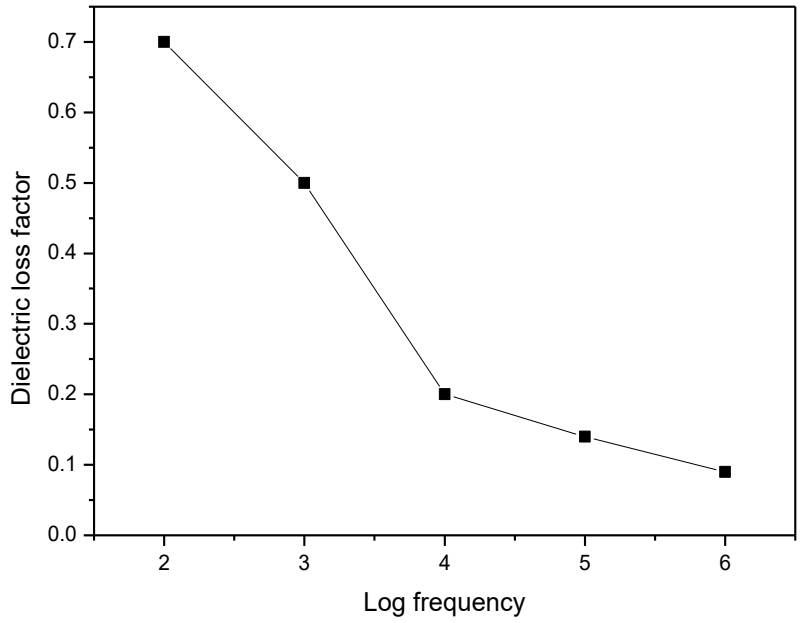
X-ray diffraction studies were carried out for the grown γ-glycine crystal using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_α (λ=0.71069 Å) radiation to obtain the crystal lattice parameters and hence to confirm the crystal structure. Hardness measurements can be defined as macro, micro and nano according to the forces applied and displacement obtained and here microhardness measurement was carried out using the Leitz microhardness tester fitted with a microscope. The Vickers hardness number (H_v) is determined using the formula $H_v = 1.8544\ P / d^2$ kg/mm^2 where *P* is the applied load in kg and *d* is the average diagonal length of the indentation mark on the crystal in mm. Values of dielectric constant and dielectric loss of the sample were determined using an LCR meter (Model:Agilent 4284A) in the frequency region 100Hz to 1 MHz and at different temperatures. The Second Harmonic Generation (SHG) conversion efficiency was measured by Kurtz and Perry powder method [17] and it was carried out using Q-switched mode locked Nd:YAG laser with first harmonic output at 1064 nm. Laser damage threshold (LDT) values for the samples were measured using an Nd:YAG laser (1064 nm, 18 ns pulse width). The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200). UV-visible transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range 200-1100 nm.

4. Electrical Properties:

Electrical properties like dielectric constant and loss factor were measured for the sample at different frequencies and temperatures. The dielectric constant in polar materials is rarely a constant, but varies with the frequency of applied field, stress, temperature and other parameters. The capacitance and dielectric loss factor (tan δ) measurements were carried out using the parallel plate capacitor method. Using the values of capacitance without sample and with sample of the capacitor, the dielectric constant was determined. The dielectric loss factor can be measured directly from the LCR meter. The variations of dielectric constant and dielectric loss with frequency for GGRC crystal are displayed in figures 2 (a) and 2(b). The values of dielectric constant and dielectric loss are observed to be decreasing with increase of frequency and hence the grown crystal shows the normal dielectric behavior. The high value of dielectric constant at low frequency region indicates the space charge polarization of the sample. The value of dielectric loss of the sample is observed to be low and this indicates the grown gamma glycine crystal has less number of defects and hence the quality of the sample is high. The low value of dielectric constant at higher frequencies will lead to increase the SHG efficiency of GGRC crystal. The temperature dependence of dielectric constant and loss factor for gamma glycine crystals are shown in the figures 3 and 4. The results show that the values of dielectric constant and loss factor increase with increase of temperature and this is due to increase of dipole moment and hence polarization in the sample when the temperature is increased. Here it is to be mentioned that as far as polarization is concerned, the increase in dielectric constant with temperature is essentially due to the temperature variation of ionic and space charge polarizations and not due to the temperature variation of orientational polarization[18-20].



(a)



(b)

Figure 2: Variations of (a) dielectric constant and (b) dielectric loss factor with frequency for gamma glycine crystal using rubidium chloride as an additive (GGRC)

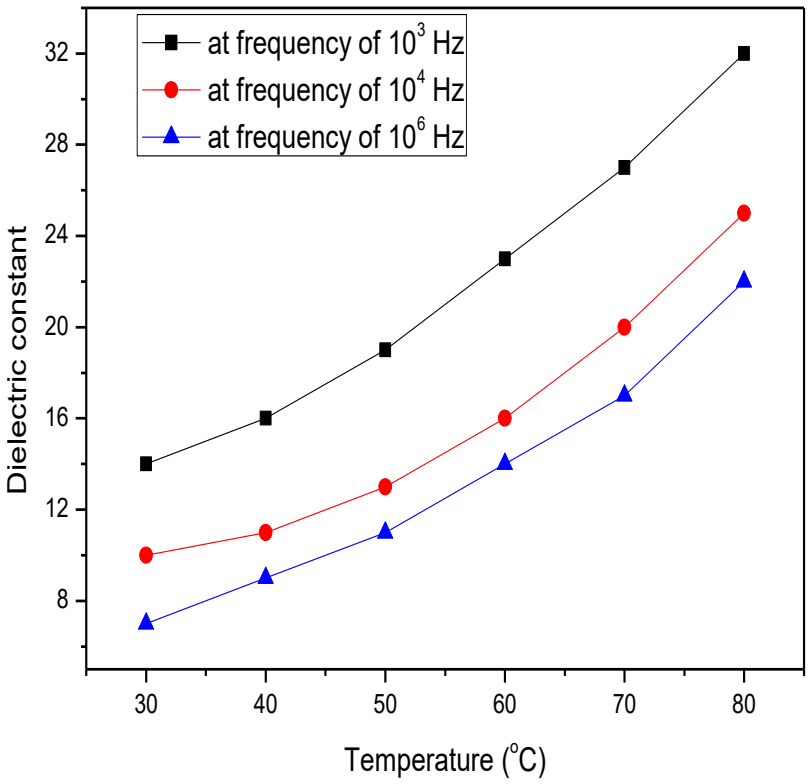


Figure 3: Variation of dielectric constant with temperature at different frequencies for GGRC crystal

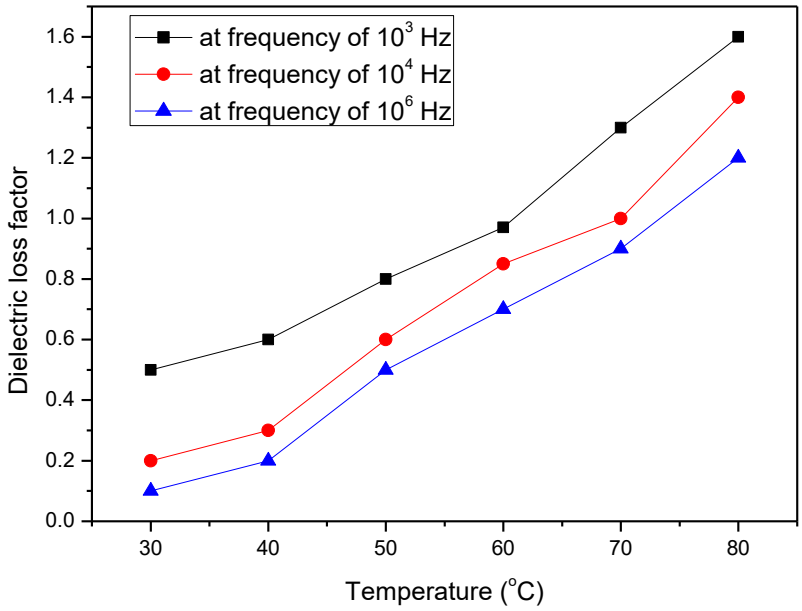


Figure 4: Variation of dielectric loss factor with temperature at different frequencies for GGRC crystal

5. X-Ray Diffraction (XRD) Studies:

The grown crystal GGRC was subjected to single crystal X-ray diffraction (XRD) studies and the crystal structure was identified. The obtained data from single crystal XRD studies are given in the table 1. From the data, it is observed that gamma glycine crystal crystallizes in the hexagonal crystal system. The obtained data are found to be in good agreement with the reported data [12]. The space group and number molecules per unit cell (Z) are noticed to be $P3_1$ and 3 respectively. When the glycine crystals are grown in the aqueous solution of rubidium chloride, the glycine molecules are regularly arranged in way such that the grown crystal crystallizes in the hexagonal system and hence gamma glycine is formed in the presence of rubidium chloride.

Table 1: Single crystal XRD data for GGRC crystal

Diffractometer	ENRAF NONIUS CAD-4
Radiation, wavelength	MoK_α, 0.71069 Å
Refinement method	Full matrix Least square method
Chemical formula	NH_2CH_2COOH
Molecular weight	75.06 g/mol
Crystal color	Colorless, transparent
Temperature	293(2) K
Symmetry	Hexagonal
Space group	$P3_1$
a	7.016 (3) Å
b	7.016 (5) Å
c	5.485(2) Å
α	90°
β	90°
γ	120°
Volume	233.62 (3) $Å^3$
Z	3
density	1.618 g/cc

6. Mechanical Parameters:

Mechanical parameters such as hardness, yield strength and stiffness constant are determined by microhardness studies. Hardness is an important solid state property and plays a vital role in device fabrication. Microhardness studies were carried out using a Vickers microhardness tester fitted with a Vickers diamond pyramidal indenter. The well polished GGRC crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied for the interval of time of 10 s. The variation of hardness number with a load for the grown crystal of gamma glycine is presented in the figure 5. The result

shows that the hardness increases with increase of the applied load and this is due to the reverse indentation size effect. Yield strength is the maximum stress that can be developed in a material without causing plastic deformation and it is the stress at which a material exhibits a specified permanent deformation. Stiffness is the rigidity of an object and its complementary concept is flexibility. Using the microhardness data, the yield strength and stiffness constant have been determined. Yield strength of the material can be found out using the relation, yield strength (σ_y) = (H_v / 3) and the stiffness constant (C_{11}) for different loads was calculated the formula $C_{11} = H_v^{7/4}$ where H_v is the microhardness of the material. The variations of yield strength and stiffness constant with the applied load for GGRC crystal are presented in the figure 6. From the results, it is observed that the yield strength and stiffness constant are increasing with increase in the applied load. As the values of yield strength, hardness and stiffness constant of gamma glycine crystal are high, sample can be used for fabrication of NLO devices such as second harmonic generator, third harmonic generator, sum frequency generator etc [21, 22].

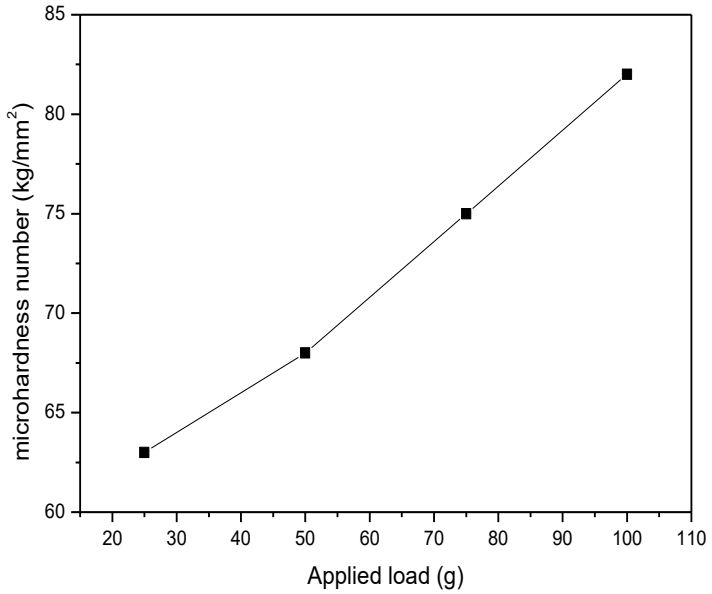


Figure 5: Plot of hardness number versus the applied load for GGRC crystal

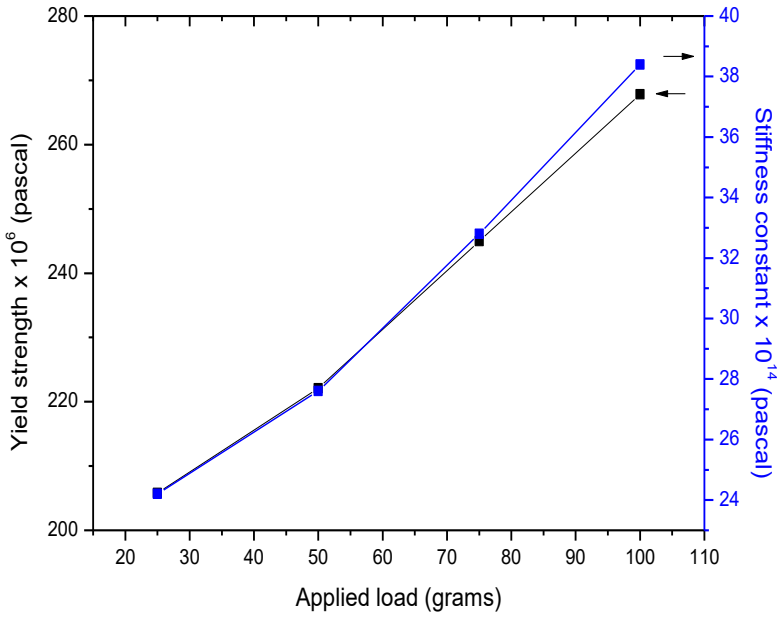


Figure 6: Plots of yield strength and stiffness constant versus the applied load for GGRC crystal

7. Measurement of Laser Damage Threshold Value:

Laser damage in a material depends upon many factors such as pulse width, repetition rate and energy of laser used. Laser damage threshold (LDT) studies for the grown crystal were performed using a Nd:YAG laser and the energy of the laser beam was measured by a coherent energy/power meter. A well polished crystal of GGRC was used for the LDT study. The value of LDT is evaluated using the relation $P= E/ \tau\pi r^2$ where τ is the pulse width in ns, E is the input energy in mJ, r is radius of the spot in mm [23]. LDT value for GGRC crystal was found to be 0.75 GW/cm^2.

8. Second Order NLO Studies:

Second harmonic generation (SHG) is one of the second order NLO properties and the study of SHG in powder form was devised by Kurtz and Perry [17]. This technique consists of a Q-switched Nd: YAG laser the output of which is filtered through 1064 nm narrow pass filter. The power of the fundamental beam is monitored by a split beam technique, in one channel of the power meter. The sample is in the form of fine powder of known grain size and pressed between two glass plates. The generated harmonic wave is passed through a 532 nm narrow pass filter and fed to other channel of the power meter. The ratio of the fundamental and harmonic intensities determines the SHG efficiency of the sample. The SHG efficiency varies with the grain size of the powdered sample. To eliminate the experimental error, urea or KDP sample of the same size is tested in the same set-up and the efficiency is evaluated as a ratio. Both the reference and test samples must have the uniform particle size of 125 to 250 microns. Throughout the experiment the laser power is kept constant. In order to improve the efficiency of second harmonic generation at the detector, a parabolic reflector is placed directly in front of the sample, (between the laser and the sample) with a small hole for the laser beam to pass through it. The SHG behaviour was confirmed from the output of the laser beam having the green emission (λ=532 nm) and thus it is a potential material for frequency conversion. The obtained value relative SHG efficiency for GGRC sample is 2.1 times that of KDP.

9. Optical Studies:

Optical studies were carried out by measuring UV-visible-NIR transmittance of the grown crystal of GGRC in the wavelength region 200-1100 nm. UV-visible transmittance spectra are attributed to a process in which the electrons of atoms or molecules absorb radiant energy and undergo transitions to higher energy levels. The wavelength at which ultraviolet absorbance maximum is found and it depends upon the magnitude of the energy involved for a specific electronic transition. A crystal of thickness of about 1.2 mm has been used in this study. The recorded UV-visible transmittance spectrum of GGRC crystal is shown in the figure 7. From the transmittance spectra, it is noticed that the crystal has a transmittance of about 80% in the visible region. In the UV region, a strong absorption is noticed at 257 nm and this corresponds to fundamental absorption of the sample. Using the formula hc / λ, the optical band gap the grown GGRC crystal is found to be 4.83 eV.

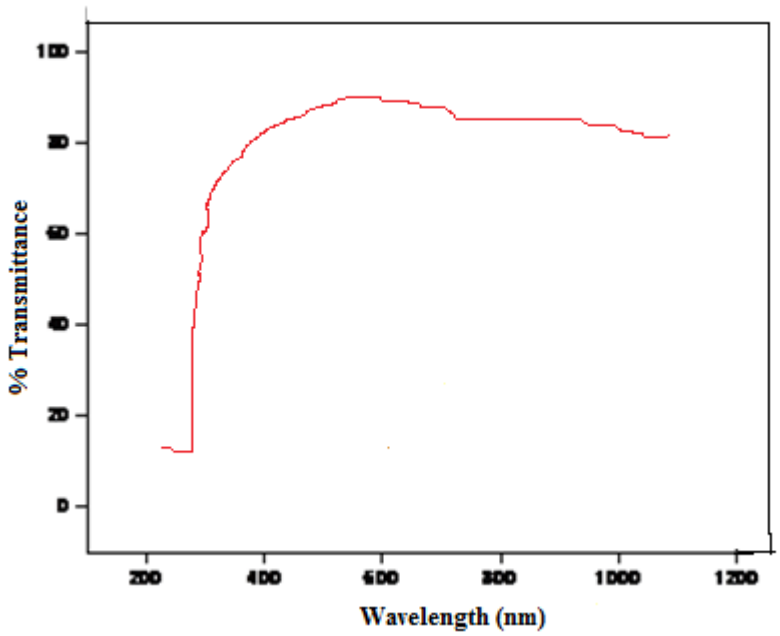


Figure 7: UV-visible-NIR transmittance spectrum of GGRC crystal

10. Conclusion:

Gamma glycine crystal was grown from the aqueous solution of rubidium chloride (GGRC) by solution method. The crystal structure of the grown crystal of γ-glycine was found to be hexagonal system. From UV-visible spectral studies, the cut-off wavelength of 257 nm for the sample was found. SHG property

studies reveal that gamma glycine crystal is a promising candidate for NLO applications and relative SHG efficiency was found to be 2.1. From Vickers microhardness studies, it is observed that the hardness number increases with the applied load and other mechanical properties such as yield strength and stiffness constant of the sample were determined. From the results of dielectric studies, it is observed that the grown crystal of GGRC has low dielectric constant and dielectric loss at higher frequencies and hence it is a suitable parameter for the enhancement of SHG coefficient. The LDT value of GGRC crystal was found to be 0.75 GW/cm^2.

11. Acknowledgement:

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