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GROWTH AND CHARACTERIZATION OF GAMMA GLYCINE CRYSTALS DOPED WITH POTASSIUM CARBONATE

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Abstract:

Undoped and potassium carbonate doped gamma glycine crystals were grown by slow evaporation technique. Gamma glycine crystals were grown from the aqueous solution of sodium chloride. 1 mole% of potassium carbonate was added into the aqueous solution of gamma glycine to obtain the doped crystals. The harvested crystals were observed to be transparent, colourless and non-hygroscopic and these crystals crystallize in hexagonal structure. FTIR studies reveal the functional groups of the samples. NLO studies have been carried out to check the second harmonic generation (SHG). Also the grown crystals were characterized by solubility studies, mechanical studies, thermal studies, dielectric and LDT studies. The results obtained from various studies are discussed.

Key Words: Gamma Glycine, Crystal Growth, Doping, Solution Method, XRD, FTIR, Dielectrics, Hardness, NLO & LDT

1. Introduction:

Glycine exhibits different distinguished forms at room temperature and under pressure. The phenomenon of a chemical substance having more than one possible crystal form is known as polymorphism. The ability of a molecule to exist in more than one solid state structure is a result of differences in the molecular packing arrangement. Many distinct polymorphic forms of glycine like alpha glycine, beta glycine, gamma glycine (□-form), deta glycine, ε-form and β'-form etc are known in the literature [1-5]. Among different forms of glycine, gamma glycine is a non-centrosymmetric crystal and it is obtained using many additives like ammonium chloride, potassium chloride, sodium chloride, cesium chloride and using especially other alkali halides. The carboxylic acid group in γ-glycine donates its proton to the amino group to form the structure ($NH_3^+CH_2COO^-$). Thus in the solid state γ-glycine exists as a dipolar ion in which carboxyl group is present as carboxylate ion and amino group present as ammonium group. The dipolar nature exhibits peculiar physical and chemical properties in gamma glycine, thus making it as ideal candidate for NLO, piezoelectric and pyroelectric applications [6-10]. In this work, gamma glycine crystals have been grown using sodium chloride as an additive. Here potassium carbonate was used as the dopant to improve the various physical and chemical properties of gamma glycine.

2. Experimental Methods:

2.1 Synthesis: Commercially purchased Analar Reagent (AR) grade chemicals like glycine, sodium chloride and potassium carbonate were used to synthesize undoped and potassium carbonate doped □-glycine (gamma glycine) salts. Glycine and sodium chloride were taken in 3:1 molar ratio and dissolved in double distilled water and stirred well using a magnetic stirrer for about 2 hours. The solution was heated at 60 ^oC until the synthesized salt of undoped □-glycine was obtained. To synthesize the potassium carbonate doped gamma glycine salt, 1 mole% of potassium carbonate was used as the dopant and it was added to the solution of □-glycine and it was also heated at 60 ^oC and stirred well till the doped sample was obtained.

2.2 Solubility and Growth of the Crystals: Solubility study was carried out using a hot plate magnetic stirrer and a constant temperature bath. By gravitational method, the solubility of the samples was determined at different temperatures. Solubility curves for undoped and potassium carbonate added γ-glycine salts at various temperatures ranging from 30 to 60^oC are presented in the figure 1. It is observed from the results that the solubility increases with temperature for both the samples and it is found to be more for potassium carbonate doped γ-glycine sample. The solubility curves are used to find the concentration of the solute in the solvent at a particular temperature and to carry out the nucleation kinetic studies. Single crystals of undoped and potassium carbonatedoped gamma glycine were grown by solution method with slow evaporation technique. Using the solubility data, the saturated solution of gamma glycine was prepared at 30$^\circ C$ and stirred well for about 2 hours. Then the solution was filtered and it was taken in a growth vessel for crystallization. In a similar manner, saturated solution of potassium carbonate doped gamma glycine was prepared and taken in separate growth vessel. The growth vessels were covered with perforated polythene papers for slow evaporation of the solvents and they were kept in a vibration free platform at room temperature (30$^\circ C$). After the growth period of 20-25 days, transparent crystals of various dimensions were harvested. The grown crystals are presented in the figures 2 and 3 and they are observed to be stable, do not decompose in air and are non-hygroscopic at ambient

temperature. The morphology of potassium carbonate doped □-glycine crystal is seemed to be different when compared to the undoped □-glycine crystal. The harvested crystals were subjected to various studies for characterization.

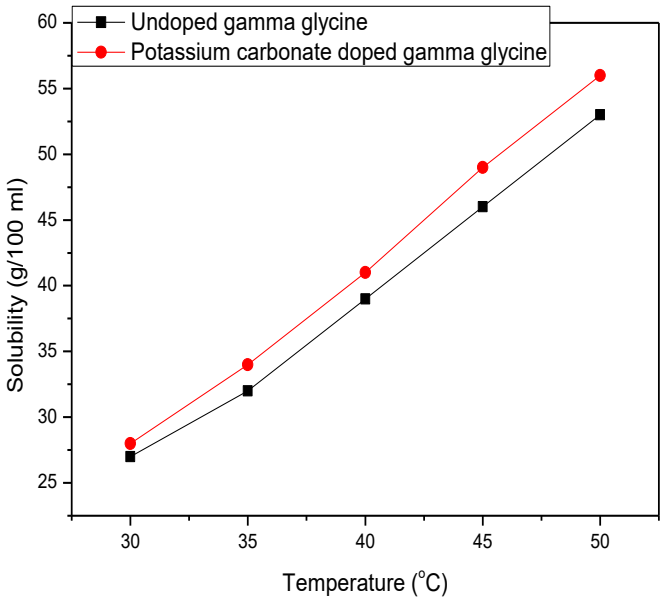


Figure 1: Variation of solubility with temperature for undoped and potassium carbonate doped gamma glycine crystals

Figure 2: The photograph of a crystal of gamma glycine

Figure 3: The photograph of a crystal potassium carbonate doped gamma glycine

3. Results and discussion

3.1 XRD Studies: X-ray diffraction (XRD) studies help us to determine the crystal structure and the lattice parameters. Single crystal X-ray diffractometric analysis was used to identify the crystal structure of the samples and it reveals that undoped and potassium carbonate doped gamma glycine crystals belong to the

hexagonal system with a non-centrosymmetric space group and thus satisfying one of the essential requirements of for the SHG activity of the crystals. The obtained lattice parameters for undoped gamma glycine are a = 7.029(4) Å, b = 7.029 (3) Å, c = 5.497 (5) Å, α = β =90°, γ = 120° and V = 233.87(3) Å^3 and the lattice parameters for potassium carbonate doped gamma glycine crystal are a = 7.045(3) Å, b = 7.045(3) Å, c = 5.514 (2) Å, α = β =90°, γ = 120° and V = 235.41(3) Å^3. The obtained lattice parameters in this work are observed to be in good agreement with the data reported in the literature [4, 11]. It is noticed that the crystal structure is not altered when gamma glycine crystal is doped with potassium carbonate. The slight changes in the lattice parameters of the doped crystal are due to incorporation of potassium carbonate into the lattice of gamma glycine crystal.

3.2 Second Order NLO Studies: Second order nonlinear optical (NLO) activity has been checked by carrying out by Second Harmonic Generation (SHG) test for the grown undoped and potassium carbonate doped gamma glycine crystals. SHG test was performed by the powder technique of Kurtz and Perry using a pulsed Nd:YAG laser(Model: YG501C, □ =1064 nm)as given in the previous chapters. Pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were used. The grown crystals were ground to powder of grain size 200-300 µm and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a capillary tube. Mirocrystalline material of Potassium Dihydrogen Phosphate (KDP) was used as reference in this experiment. Second Harmonic Generation (SHG) from the samples was detected using an optical cable attached to a fluorescence spectroscope (Model: DID A-512 G/R). The values of measured SHG efficiency for undoped and potassium carbonate doped gamma glycine crystalline materials are 1.42 and 1.57 respectively. From the literature, it is found that the value of SHG efficiency of gamma glycine crystal grown in the aqueous solution of lithium bromide is 3 and that for gamma glycine crystal grown in the aqueous solution of sodium fluoride is 1.3 [12,13]. Since the values of SHG efficiency of the undoped and potassium carbonate doped gamma glycine crystals are more than one, they are good candidates for NLO device applications.

3.3 Determination of Mechanical Properties: Mechanical properties such as hardness, yield strength and stiffness constant of the samples have been determined for the samples by carrying out microhardness studies. Microhardness studies for any system have a direct correlation with crystal structure and are very sensitive to the presence of any other phase or phase transition and lattice perfections prevalent in the system and hardness of a crystal depends upon many parameters like interatomic spacing, bond length, bond energy, positions of the atoms in the lattice etc. Yield strength is the maximum stress that can be developed in a material without causing plastic deformation and stiffness constant is a measure of resistance of plastic to bending and tightness of bonding between neighboring atoms. Using a Vickers microhardness tester, the hardness number is determined using the relation $H_v = 1.8544\ P / d^2$ where, 'P' is the applied load in kilogram and 'd' is the average diagonal length of the indentation in millimetre.

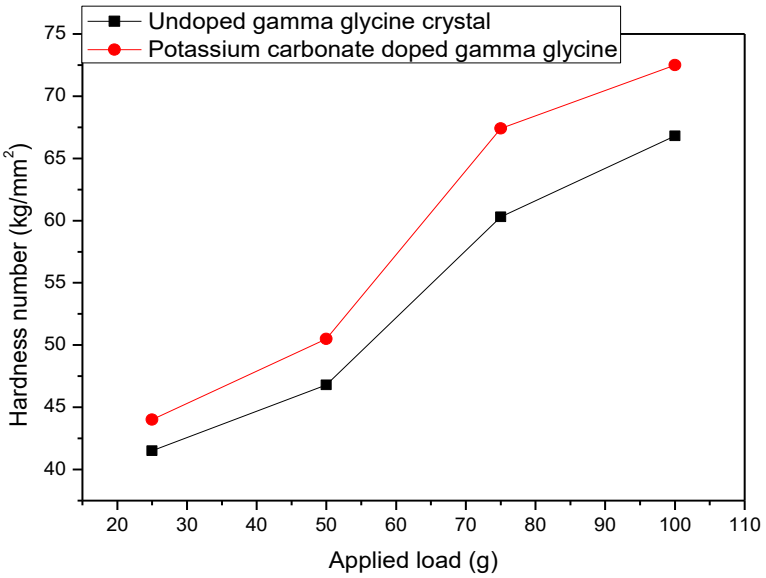


Figure 4: Plots of hardness number versus the applied load for undoped and potassium carbonate doped gamma glycine crystals

Yield strength of the crystal is determined using the relation $\sigma_y = (H_v/3)$ where σ_y is the yield strength and H_v is the microhardness of the material. The stiffness constant (C_{11}) for different loads is calculated using Wooster's empirical formula given by $C_{11} = H_v^{7/4}$ [14-16]. The variations of hardness number with the applied load are given in the figure 4. The results show that for both the samples, the hardness is found to be increasing with

increase of the applied load and the hardness is observed to be more when gamma glycine crystals are doped with potassium carbonate. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed which is due to the reverse indentation size effect. It is noticed that there are cracks found in the crystals when the load applied is more than 100 g. The values of yield strength and stiffness constant are determined and are provided in the tables 1 and 2. The results show that both yield strength and stiffness constant are observed to be increasing with increase of the applied load for undoped and potassium carbonate doped gamma glylcine crystals. Since the values of yield strength and stiffness constant are high, the bond strength between atoms in the crystal lattices of the grown crystals is strong and this leads to usage of these crystals in the fabrication of NLO devices.

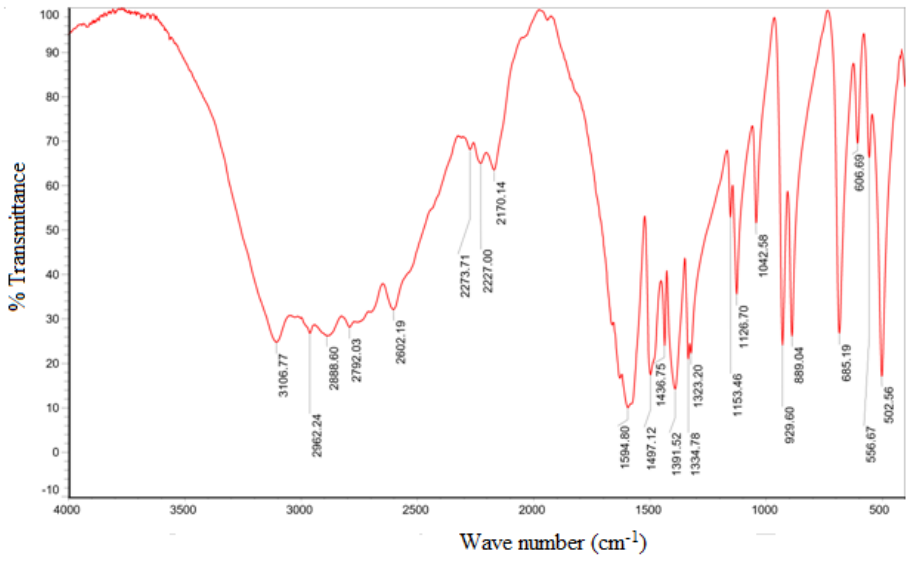
Table 1: Values of yield strength for undoped and potassium carbonate doped gamma glycine crystals

Applied load (grams)	Yield strength x 10^6 (N/m^2)	
	Undoped gamma glycine crystal	Potassium carbonate doped gamma glycine crystal
25 g	135.56	143.68
50	152.78	164.90
75 g	196.88	220.21
100 g	218.23	236.78

Table 2: Values of stiffness constant for undoped and potassium carbonate doped gamma glycine crystals

Applied load (grams)	Stiffness constant x 10^{14} (N/m^2)	
	Undoped gamma glycine crystal	Potassium carbonate doped gamma glycine crystal
25 g	11.62	12.86
50	14.42	16.41
75 g	22.42	27.22
100 g	26.76	30.87

3.4 FTIR Studies for Identification of Functional Groups: FTIR spectra were recorded using a Fourier Transform mathematical formulated spectrophotometer (Model: SHIMADZU- FTIR-8400S) with a KBr pellet technique for the grown undoped and potassium carbonate doped gamma glycine crystals and they are presented in the figures 5 and 6. FTIR spectra are used to identify the various functional groups present in the samples. The small bands/peaks in the region between 3400- and 2600 cm^{-1} are due to hydrogen interaction with other atoms such as NH_3^+ stretching, OH stretching and C–H stretching. The carboxyl group is present as carboxylate ion and amine group exists as ammonium ion in the undoped and potassium carbonate doped gamma glycine crystals. The presence of carboxylate and ammonium ions clearly indicates that the glycine molecule exists in zwitter ionic form. When gamma glycine is doped with potassium carbonate, there are slight changes in the absorption bands/peaks and this indicates that the dopant has entered into the lattice of gamma glycine crystals. The FTIR spectral absorption frequencies and their assignments given in the tables 3 and 4. The peaks/bands of FTIR spectra of the samples are given assignments using the data as given in the literature [17-19].



Figurre 5: FTIR spectrum of gamma glycine crystal

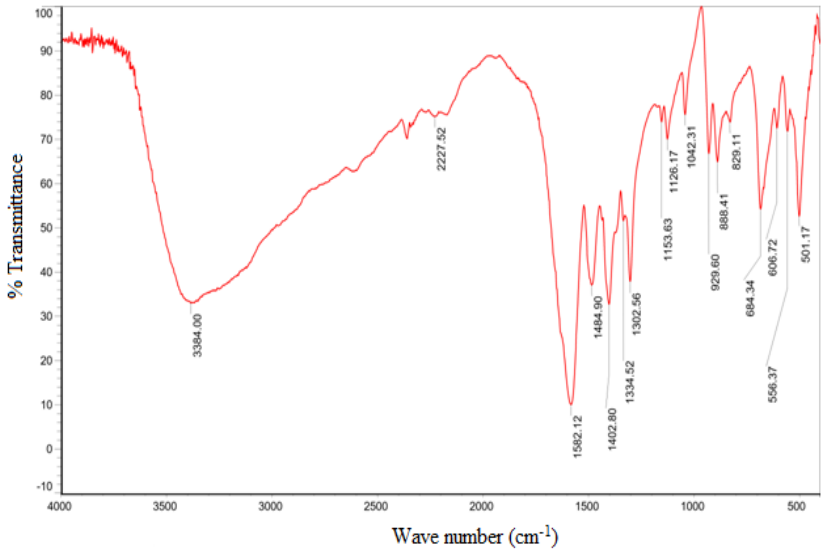


Figure 6: FTIR spectrum of potassium carbonate doped gamma glycine crystal

Table 3: FTIR spectral assignments for undoped gamma glycine crystal

Absorption frequencies (cm^{-1})	FTIR assignments
3106	NH_3^+ stretching
2962	N-H-O stretching
2227	Combination band
1582	COO^- stretching
1484	NH_3^+ deformation
1402	CH_2 bending
1334	CH_2 twisting
1042	CCN stretching
929	CH_2 rocking
888	C-C stretching
684	COO^- bending
606	COO^- wagging
556	NH_3^+ torsion
501	COO^- rocking

Table 4: FTIR spectral assignments for potassium carbonate doped gamma glycine crystal

Absorption frequencies (cm^{-1})	FTIR assignments
3500-3100	NH_3^+ stretching and OH stretching
2962	N-H-O stretching
2600	CH stretching
2227	CH_2 stretching
1594	COO^- stretching
1497	NH_3^+ deformation
1491	CH_2 bending
1334	CH_2 twisting
1042	CCN stretching
929	CH_2 rocking
889	C-C stretching
685	COO^- bending
606	COO^- wagging
556	NH_3^+ torsion
502	COO^- rocking

3.5 Thermogravimetric Analysis: Thermal analysis measures the physical property of the substance as a function of temperature while the substance is subjected to a controlled temperature program. The thermogravimetric (TG) analysis for potassium carbonate doped gamma glycine crystal was carried out from 25 ^oC to 700 ^oC at the heating rate of 10 ^oC/min in the nitrogen atmosphere using the instrument NETZSCHSTA 409C/CD. The sample weighing 5.015 mg was taken for the measurement. The recorded TG curve of the sample crystal is shown in the figure 7. In the TG trace, there is almost no mass change upto 200 ^oC and a mass change of 40 % occurs in the temperature region of 200 ^oC - 275 ^oC due to decomposition of the sample. A mass

change of 25% occurs in next temperature region of 275-700 ^{o}C and this is due to further decomposition of the sample. From this study, it is confirmed that the sample is thermally stable upto 200 ^{o}C and this ensures the suitability of the material for applications in lasers where the crystal is required to withstand high temperature.

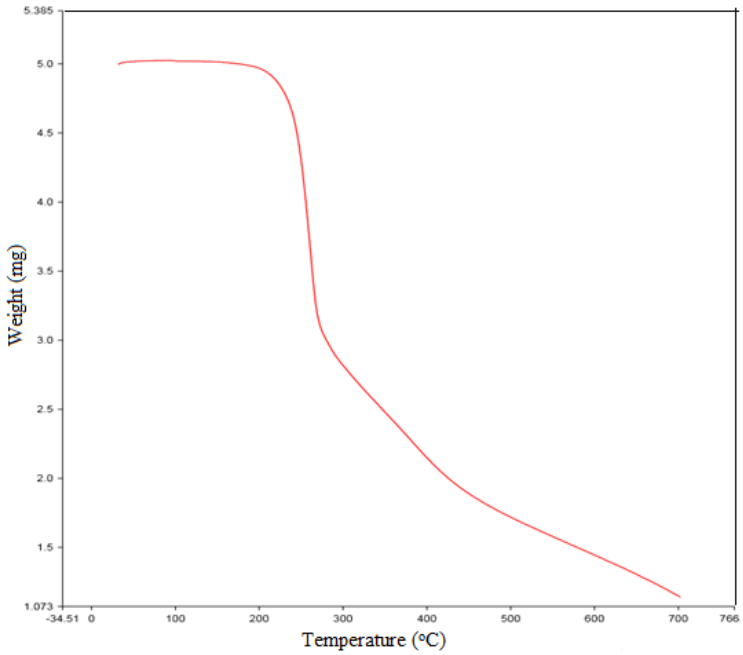


Figure 7: Thermogravimetric (TG) curve for potassium carbonate doped gamma glycine crystal

3.6 Dielectric Properties: Dielectric properties like dielectric constant, loss factor and dielectric strength etc are interconnected with electro-optic properties of the crystal. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystal. Smooth surface of a sample was selected and coated with graphite for the experiment. The dielectric constant (ε_r) and dielectric loss (tan δ) were measured for different frequencies and temperatures using an LCR meter and their variations with frequencies for different temperatures are shown in figures 8 and 9. From the results, it is observed that ε_r and tan δ are high at low frequencies and decreases to constant value as the frequency is increased. The high value of ε_r at low frequencies may be due to the presence of space charge and dipolar polarizations. At low frequencies, the dipoles can easily switch alignment with the changing fields. As the frequency increases, the dipoles are able to rotate less and maintain phase with the field and thus they reduce their contribution to the polarization field and reduces the dielectric constant and dielectric loss.

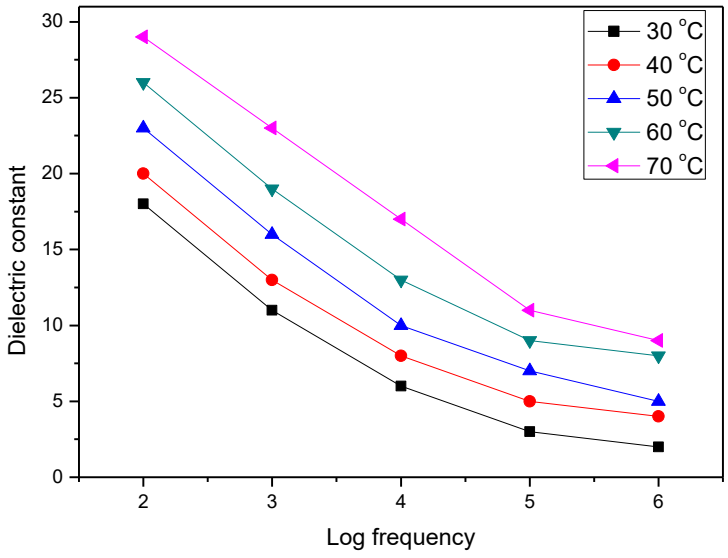


Figure 8: Frequency dependence of dielectric constant at different temperatures for undoped gamma glycine crystals

Beyond certain frequency of the electric field, the dipole does not follow the alternating field. Variation of the dielectric parameters with temperature is generally attributed to the crystal expansion, the electronic, space charge and ionic polarizations and also attributed to the thermally generated charge carriers and impurity dipoles. The low dielectric loss at high frequency implies that the grown crystals possess good quality with low concentration of defects [20, 21]. The dielectric constant and loss factor were measured for potassium carbonate doped gamma glycine crystal and the results are presented in the figures 10 and 11. The results show that the dielectric parameters also decrease with increase of frequency and increase with increase of temperature for potassium carbonate doped gamma glycine crystal.

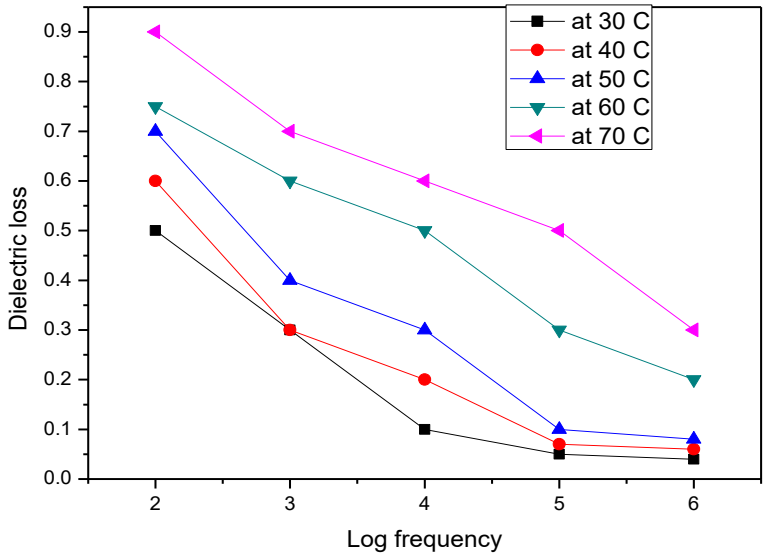


Figure 9: Frequency dependence of dielectric loss at different temperatures for undoped gamma glycine crystals

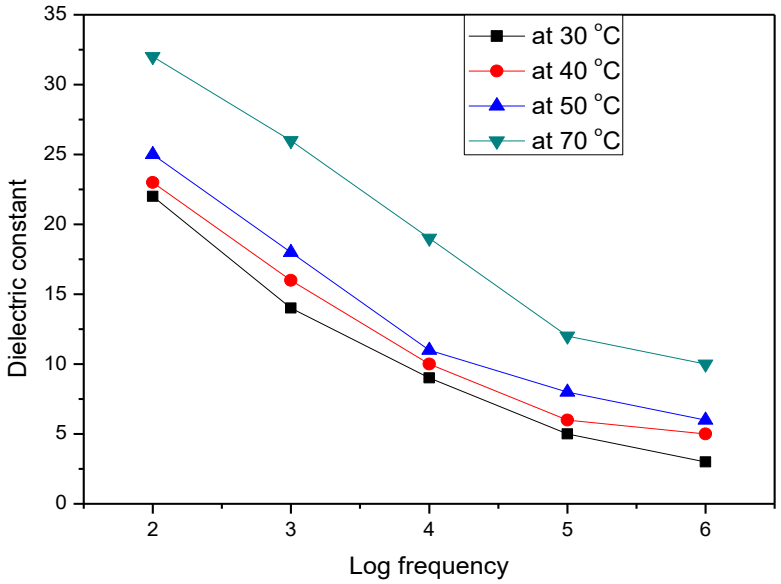


Figure 10: Frequency dependence of dielectric constant at different temperatures for potassium carbonate doped gamma glycine crystals

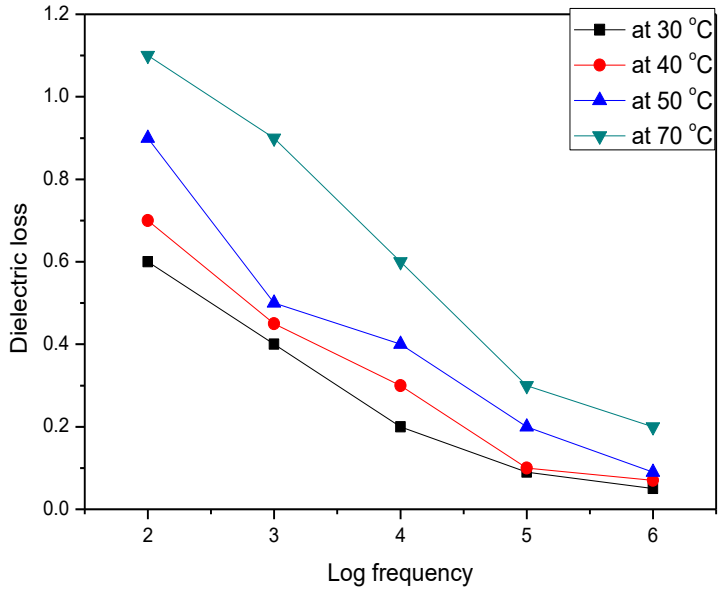


Figure 11: Frequency dependence of dielectric loss at different temperatures for potassium carbonate doped gamma glycine crystals

3.7 Measurement of Laser Damage Threshold (LDT): The optical damage threshold of an optical crystal is an important factor that hinders its applications. Optical damage threshold studies have been carried out for sample crystals using Q switched Nd: YAG laser of pulse width 10 nano seconds and repetition rate of 10 Hz. The laser beam was focused and the sample was moved step by step into the focus along the optical axis of the crystal. Laser damage threshold (LDT) value is found to be 0.647 GW/cm^2 for undoped gamma glycine crystal and LDT value is found to be 0.702 GW/cm^2 for potassium carbonate doped gamma glycine crystal.

4. Conclusions:

Unodped and potassium carbonate doped gamma glycine crystals were synthesized and single crystals were grown by solution method. Solubility is found to be increasing with increase of temperature for both the samples. The crystal structure was identified by XRD studies and the functional groups of the samples were identified by FTIR studies. The mechanical parameters such as hardness, yield strength and stiffness constant were determined at different applied loads. Dielectric parameters such as dielectric constant and loss factor were observed to be decreasing with frequency and increasing with increase of temperature. The LDT and SHG values for the samples were measured and it is observed that these values are more for potassium carbonate doped gamma glycine crystal than that of undoped sample.

5. Acknowledgement:

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