

# Growth and studies of gamma-glycine crystals doped with zinc sulfate

T.Gladys Vimala, E.Bena Jothy, P.Selvarajan

**Abstract**— Single crystals of undoped and zinc sulphate doped gamma-glycine crystals were grown by slow evaporation solution growth technique using water as the solvent. Undoped gamma-glycine salt was prepared by using alpha-glycine and sodium chloride. 1 mole% of zinc sulfate was added as the dopant to the gamma-glycine to prepare the doped sample. Solubility of the samples was measured using water as the solvent at different temperatures. The grown crystals of undoped and zinc sulfate doped gamma-glycine were harvested after a growth period of 30 days. The lattice parameters were found by XRD method. The relative SHG efficiency was measured for both the samples by Kurtz-Perry method. Hardness parameters were determined at different applied loads. Dielectric behavior of the samples was studied by measuring dielectric constant and loss factor at various frequencies and temperatures. LDT studies were carried out for the samples to find the laser damage threshold values. Photoconductivity was measured for the samples at different applied electric fields.

**Index Terms**— Characterization, doping, gamma-glycine, single crystal, solution growth

## I. INTRODUCTION

Crystals of amino acids have potential applications in optical communication, photonics, optical computing, electro-optic modulation, optical image processing etc. Glycine is the simplest amino acid which is available in many forms like  $\alpha$ -glycine,  $\beta$ -glycine and  $\gamma$ -glycine. Gamma-glycine ( $\gamma$ -glycine) crystallizes in a non-centrosymmetric space group and hence it possesses nonlinear optical (NLO) and piezoelectric properties[1-3]. Gamma-glycine crystals can be grown using many alkali halides like sodium chloride, potassium chloride, lithium chloride, potassium bromide etc. In the normal atmosphere, gamma-glycine exists as a dipolar ion in which carboxyl group is present as a carboxylate ion and amino group is present as ammonium ion. The  $\gamma$ -form of glycine is thermodynamically the most stable form at room temperature but transforms to the  $\alpha$ -form at high temperatures (165–175° C). The growth of  $\gamma$ -form of glycine crystals can be done from aqueous solution or gel in the presence of additives, from supersaturated solution irradiated with plane-polarized laser light, or from surfactant based microemulsion and lamellar phases[4-5]. The effect of additives has been investigated on the crystal morphology and polymorphism of glycine and it was explained that the crystallization of the least stable

$\beta$ -form and the stable  $\gamma$ -form from aqueous solution correlated with conditions that had inhibitory effects on the dimer formation[6,7]. In this work,  $\gamma$ -glycine crystals were grown by solution method using sodium chloride as an additive. It has been reported that doping NLO crystals with organic impurities can alter various physical and chemical properties and doped NLO crystals may have improved properties. To alter the properties of gamma-glycine crystals, zinc sulfate has been introduced as the dopant and the grown crystals have been subjected to many studies like XRD studies, SHG, LDT studies, microhardness studies, dielectric and photoconductivity studies and the obtained results are discussed.

## II. GROWTH AND SOLUBILITY

AR grade of glycine and sodium chloride in the molar ratio of 3:1 were used for growth of  $\gamma$ -glycine crystal. The calculated amounts of glycine and sodium chloride were dissolved in double distilled water and stirred well using a magnetic stirrer for about 2 hours and the solution was filtered using 4 micro Whatmann filter papers. Then the filtered solutions were kept in a growth vessel covered with a porous paper. By slow evaporation of solvent at ambient temperature, single crystals of gamma-glycine were obtained. The crystals were harvested after a period of about 30 days. To harvest the zinc sulfate doped gamma-glycine crystals, 1 mole% of zinc sulfate was added into the solution of gamma-glycine and the doped crystals were obtained after a growth period of about 35 days. Solubility was measured for both undoped and zinc sulfate doped gamma-glycine crystals by gravimetric method [8]. The variations of solubility with temperature for the samples 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 zinc sulfate doped  $\gamma$ -glycine crystal. Since solubility increases with temperature, the samples of this work have positive temperature coefficient of solubility. The increase in solubility for the zinc sulfate doped crystal is responsible for morphological change and hence the undoped and doped crystals have the different morphology.

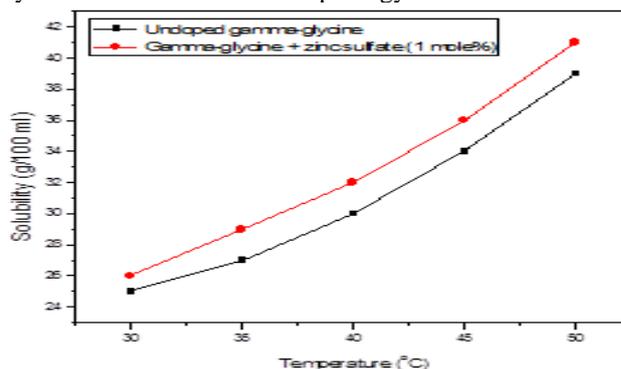


Fig.1: Variation of solubility with temperature for undoped and zinc sulfate doped gamma-glycine crystals

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III. RESULTS AND DISCUSSION

A. X-Ray Diffraction Studies

The grown single crystals were subjected by single crystal XRD studies using an ENRAF NONIUS CAD4 diffractometer with MoK $\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ) and the obtained data are presented in the table 1. From the data, it is observed that the grown crystals crystallize in hexagonal system with the space group P3 $_2$ . The number of molecules per unit cell (Z) for both crystals of this work is found to be 3. The unit cell parameters of pure  $\gamma$ -glycine obtained in this work are very close agreement with reported work [9] and slight changes of lattice parameters have been noticed for the zinc sulfate doped sample compared to pure  $\gamma$ -glycine crystal. The changes in the lattice parameters are due to incorporation of zinc sulfate in the lattice of  $\gamma$ -glycine crystal.

Table 1: XRD data for undoped and zinc sulfate doped  $\gamma$ -glycine crystals

Sample	Cell parameters	Volume ( $\text{\AA}^3$ ) <sup>3</sup>
Undoped $\gamma$ -glycine crystal	a = 7.043(3) $\text{\AA}$ b = 7.043(3) $\text{\AA}$ c = 5.494(1) $\text{\AA}$ $\alpha = 90^\circ, \beta = 90^\circ$ $\gamma = 120^\circ$	236.01(2)
Zinc sulfate doped $\gamma$ -glycine crystal	a = 7.051(4) $\text{\AA}$ b = 7.051(4) $\text{\AA}$ c = 5.512(2) $\text{\AA}$ $\alpha = 90^\circ, \beta = 90^\circ$ $\gamma = 120^\circ$	237.32(3)

B. SHG studies

Second Harmonic Generation (SHG) test for the grown pure and zinc sulfate doped gamma-glycine crystals was performed by the powder technique of Kurtz and Perry [10] using a pulsed Nd:YAG laser (Model: YG501C,  $\lambda=1064 \text{ nm}$ ). 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 500-600  $\mu\text{m}$  and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a capillary tube. Microcrystalline 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 spectroscopy (Model: DID A-512 G/R). The measured SHG efficiency values for pure and zinc sulfate doped  $\gamma$ -glycine samples are 1.86 and 1.98 times as that of KDP. When  $\gamma$ -glycine crystals are doped with zinc sulfate, it is noticed that the SHG efficiency is increased and hence the zinc sulfate doped crystals are the better NLO materials.

C. Microhardness studies

The hardness of a material is a measure of its resistance to plastic deformation. Hardness studies of the grown crystals were carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study on both pure and zinc sulfate doped gamma-glycine crystals. Indentations were made for various loads from 25 g to 100 g. Several trials of indentation

were carried out on the prominent face and the average diagonal lengths were measured for an indentation time of 10 seconds. The Vickers microhardness number was calculated using the relation  $H_v = 1.8544 P/d^2 \text{ kg/mm}^2$  where P is the applied load and d is the diagonal length of the indentation impression. Figure 2 shows the variation of hardness number with different loads for pure and zinc sulfate doped  $\gamma$ -glycine crystalline samples and it is noticed that Vickers hardness number ( $H_v$ ) increases with the applied load up to 100 g and cracks start developing beyond 100 g around the indentation mark. From the results, it is observed that the hardness of  $\gamma$ -glycine crystal increases when it is doped with zinc sulfate. This increase in the hardness value of doped sample can be attributed to the incorporation of impurity in the lattice of  $\gamma$ -glycine crystal. The addition of zinc sulfate to  $\gamma$ -glycine crystalline sample most probably enhances the strength of bonding with the host material and hence hardness number increases [11].

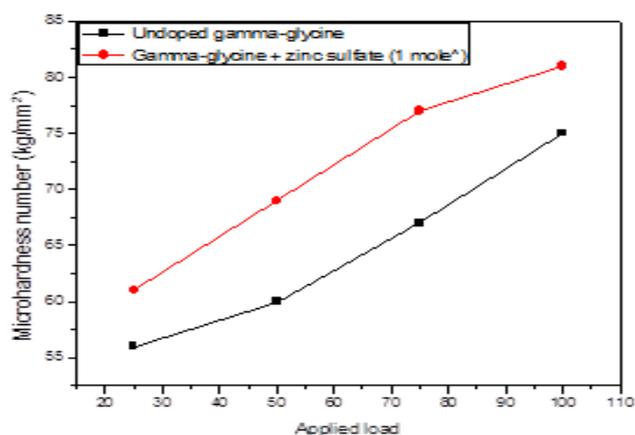


Fig.2: Variation of hardness number with the applied load for undoped and zinc sulfate added gamma-glycine crystals

D. Dielectric studies

The dielectric parameters like dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan \delta$ ) are the basic electrical properties of solids. Measurements of dielectric properties of grown crystals were carried out using an LCR meter at various frequencies in the range  $10^2 - 10^6 \text{ Hz}$  and at different temperatures. The variations of the dielectric constant and loss factor with frequency for undoped and zinc sulfate doped gamma glycine crystals at room temperature are presented in Figs.3 and 4. The obtained results suggest that the dielectric constant and loss strongly depend on the frequency of applied field. It is observed from the figures that both dielectric constant and loss are high at low frequencies and decrease with increase in frequency, attaining almost constant values beyond  $10^4 \text{ Hz}$ . Higher values of dielectric constant and dielectric loss of zinc sulfate doped gamma glycine crystals at low frequencies are due to space charge polarization. It is to be noted here that space charge polarization is dominant and electronic and ionic polarizations are not very much active in low frequency region. The nature of decrease of  $\epsilon_r$  and  $\tan \delta$  with frequency suggests that the crystals of this work seem to contain dipoles of continuously varying relaxation times. Since the dipoles of larger relaxation times are not able to respond to the higher frequencies, the dielectric constant and loss tangent are low at higher frequencies [13].

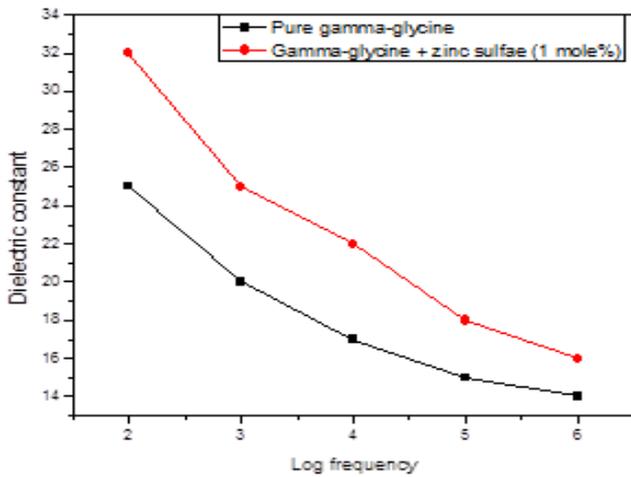


Fig.3: Frequency dependent dielectric constant for undoped and zinc sulfate doped gamma-glycine crystals

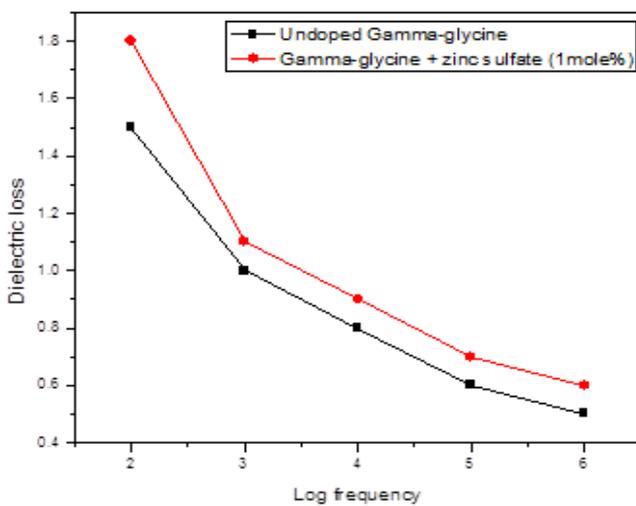


Fig.4: Frequency dependent dielectric loss factor for undoped and zinc sulfate doped gamma-glycine crystals

#### E. Laser damage threshold (LDT) studies

The laser damage in the crystals are caused by various physical processes such as electron avalanche, multiphoton absorption and photoionization for the transparent materials whereas in case of high absorbing materials, the damage threshold is mainly due to the temperature rise, which leads to strain-induced fracture. It also depends upon the specific properties of material, pulse width, and wavelength of laser used. Laser damage threshold (LDT) studies for the samples were carried out 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). LDT value is determined using the formula  $P = E / \tau \pi r^2$  where  $\tau$  is the pulse width in ns,  $E$  is the input energy in mJ,  $r$  is radius of the spot in mm [13]. The LDT value is one of the important device related properties of NLO crystals. LDT value is the maximum permissible power that can withstand in a particular crystal. The obtained values of LDT of the undoped and zinc sulfate added gamma-glycine crystals are 0.651 GW/cm<sup>2</sup> and 0.722 GW/cm<sup>2</sup> respectively. From the results, it is observed that the values of laser damage threshold are more for the zinc sulfate added gamma-glycine crystal than that of undoped crystal. The increase of LDT values are due to increase of bond strength when gamma-glycine crystals are doped with zinc sulfate.

#### F. Photoconductivity

Photoconductivity is caused by an increase in the concentration of charge carriers when UV or visible light is incident on a semiconductor/insulator. Photoconductivity studies have been carried out using a photoconductivity set-up with a Keithley 485 picoammeter at room temperature. By connecting the sample in series to a DC power supply and a picoammeter, the dark conductivity of the sample was studied. Electrical contacts were made on the samples using the silver paint. In order to measure the photo current, the sample was illuminated with a halogen lamp by focusing a spot of light on the sample with the help of a convex lens. Photocurrents and dark currents were measured for the samples at different applied DC voltages. The variations of dark and photo currents for undoped and zinc sulfate doped gamma-glycine crystals are shown the figure 5. It is noticed that the values of dark current and photo current increase with increase of applied electric field. For the samples, it is observed that the photo current is more than dark current and hence the samples have positive photoconductivity. The positive photoconductivity of the samples is due to increase of charge carriers when light is passed onto the samples. When gamma-glycine crystals are doped with zinc sulfate, there is an increase of dark and photocurrents and this is due to incorporation of the dopant (zinc sulfate) into the host gamma-glycine crystals.

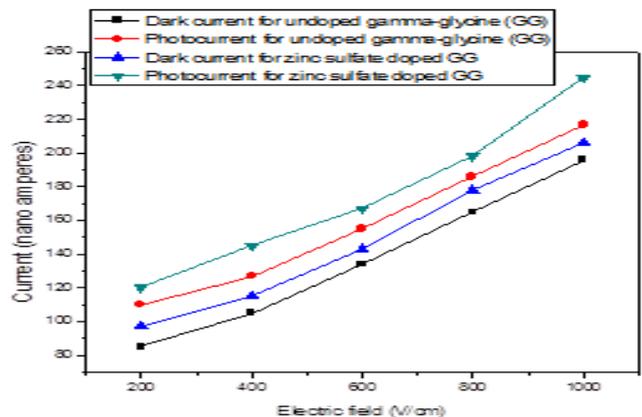


Fig.5: Variations of photocurrent and dark current with the applied field for undoped and zinc sulfate doped gamma-glycine crystals

#### IV. CONCLUSION

Single crystals of undoped and zinc sulfate added gamma-glycine were grown by slow evaporation technique at room temperature. The solubility of the samples has been measured and it increases with increase in temperature for both the samples. The XRD studies reveal the hexagonal structure of the samples. The dielectric constant and loss factor were measured for the samples at various frequencies at room temperature and these values are observed to be increasing when gamma-glycine crystals are doped with zinc sulfate. The hardness of gamma-glycine crystal is observed to be increasing when zinc sulfate is added as the dopant into the host crystal. The SHG and LDT values of the samples were measured and it is noticed that there are significant changes when gamma-glycine crystals are added with zinc sulfate. Photocurrents and dark currents have been measured for the samples and this study reveals that the samples are positive photoconductors [14,15].

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## REFERENCES

- [1] B. Narayana Moolya, A. Jayarama, M.R. Sureshkumar, S.M. Dharmaparakash, *J.Crystal Growth* 280 (2005) 581.
- [2] Jan Baran, Henryk Ratajezak, *Spectrochimica Acta Part A* 61 (2005) 1611.
- [3] K. Srinivasan *J. Crystal Growth* 311 (2008) 156.
- [4] J. Zaccaro, J. Matic, A.S. Myerson, B.A. Garetz, *Cryst. Growth Des.* 1 (2001) 5.
- [5] K. Allen, R.J. Davey, E. Ferrari, C. Towler, G.J. Tiddy, *Cryst. Growth Des.* 2 (2002) 523.
- [6] C.S. Towler, R.J. Davey, R.W. Lancaster, C.J. Price, *J. Am. Chem. Soc.* 126 (2004) 13347.
- [7] G.D. Profio, S. Tucci, E. Curcio, E. Drioli, *Cryst. Growth Des* 7 (2007) 526.
- [8] A.S.J. Lucia Rose, P. Selvarajan, S. Perumal, *Spectrochimica Acta Part A* 81 (2011) 270.
- [9] Y. Iitaka, *Acta Crystallogr.* 14 (1961) 1.
- [10] S.K.Kurtz, T.T.Perry, *J.Appl.Phys.* 39 (1968) 3798.
- [11] K. Boopathi, P.Ramasamy, G.Bhagavannarayana, *Journal Crystal Growth* 386(2014)32-37.
- [12] U. Von Hundelshausen, *Phys. Lett.* 34A (1971) 7.
- [13] Redrothu Hanumantharao, S.Kalainathan, *Optik*, 124 (2013) 2204.
- [14] R. H. Bube, "Photoconductivity of solids," Wiley, New York, 1981.
- [15] Sagadevan Suresh, *J. Crystallization Process and Technology*, 3 (2013)87-91.

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