

Studies of Undoped Glycine, Cesium Chloride Doped Glycine and Rubidium Chloride Doped Glycine Crystals

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Abstract- Glycine is one of the simplest amino acid that has no asymmetric carbon atom and is optically inactive. It is mixed with other organic or inorganic salts and acids to obtain new complexes and these complexes have improved chemical stability, thermal, optical, mechanical, electrical, linear and nonlinear optical properties. Many glycine based crystals are known to be having interesting properties and in this work, cesium chloride and rubidium chloride are separately added in small amounts into the lattice of glycine crystals to get the doped samples for the research work. Single crystals of undoped, cesium chloride doped and rubidium chloride doped glycine were grown by solution method and grown crystals were analyzed by various characterization techniques. Solubility was measured for the samples. XRD study was carried out to find the crystal structure and hardness study was done on the crystals to find the mechanical strength. Second harmonic generation studies were carried out to find SHG efficiency. Density and structural characterization was performed for the samples. Photoconductivity studies were carried out for the samples and the results are discussed.

Index terms: Doping, glycine, crystal growth, characterization, XRD, hardness

I. INTRODUCTION

Many researchers are actively involved in using amino acids like glycine, L-alanine, L-arginine, L-histidine, L-threonine, L-proline etc to prepare novel second-order and third-order NLO crystals for usage in laser, optical and photonic technologies [1-5]. Among amino acids, glycine has the non-chiral zwitterionic form and it crystallizes in six different polymeric forms viz. α , β , γ , δ , ϵ and β' -forms. α -glycine has no asymmetric carbon atom and is optically inactive. It has been reported that glycine combines with sulphuric acid, nitric acid, calcium chloride, calcium nitrate, barium chloride, silver nitrate, phosphoric acid, lithium sulfate, sodium nitrate, hydrochloric acid etc to form useful single crystals [6-10]. Complexes of glycine with inorganic salts which crystallizes in non-centrosymmetric space group have been reported to be promising materials for SHG. Glycine silver nitrate, glycine hydrogen nitrate, glycine hydrogen phosphate, glycine lithium sulphate, glycine zinc sulphate, glycine zinc chloride, diglycine manganese chloride and triglycine fluoroberrylate are some of the complexes of

glycine which have been synthesized to grow single crystals and characterize them [11-14].

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 form β and the stable form γ from aqueous solution correlated with conditions that had inhibitory effects on the dimer formation, thus inhibiting the spontaneous nucleation of the α -form [15]. Profio *et al.* studied the selective nucleation of α - and γ -forms of glycine by using microporous membranes [16]. Recently, various studies on potassium nitrate doped glycine crystals were reported in the literature [17].

II. EXPERIMENTAL

A. Growing Crystals

AR grade chemicals such as glycine, cesium chloride and rubidium chloride were purchased commercially from Merck India. Double distilled water was prepared using the double distillation plant and it was used for synthesis and growth of crystals. Three samples viz. (i) undoped glycine, (ii) cesium chloride doped glycine and rubidium chloride doped glycine were prepared here. Single crystals of these samples were grown by solution method with slow evaporation technique. To get the doped samples, 2 mole% of cesium chloride and rubidium chloride were added separately into glycine. Saturated solutions of undoped glycine, rubidium chloride doped glycine (RCG) and cesium chloride doped glycine (CCG) were prepared in three different beakers using the double distilled water as the solvent. The prepared solutions were stirred well for about 3 hours using a hot plate magnetic stirrer and were filtered. The filtered solutions were taken in three different growth vessels and covered with perforated sheets for slow evaporation. Quality crystals were harvested after a growth period of 30 days and the photograph of the grown crystals is shown in the figure 1.

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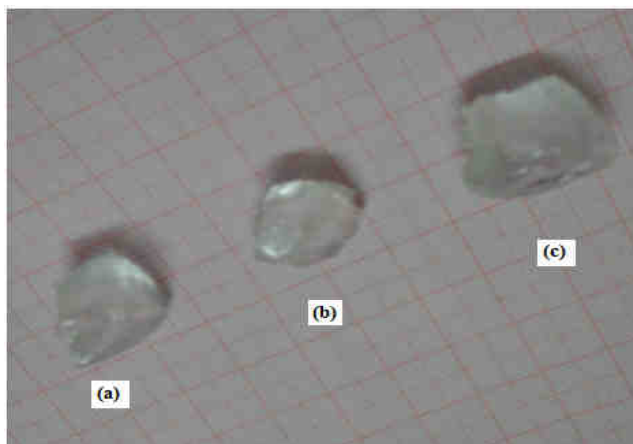


Fig.1: Grown crystals of (a) glycine, (b) cesium chloride doped glycine (CCG) and (c) rubidium chloride doped glycine (RCG)

B. Characterization techniques

Single crystal XRD data of the samples were obtained using ENRAF CAD-4 X-ray diffractometer with MoK_α ($\lambda=0.71069 \text{ \AA}$) radiation. The powder XRD pattern of the sample was recorded on a microprocessor controlled X-ray diffractometer using nickel filtered CuK_α radiation. The microhardness studies for the grown crystals were carried out using a SHIMADZU HMV-2000 microhardness tester fitted with a Vickers diamond pyramid indenter. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm. Density was measured by floatation method. Vickers hardness tester was used to measure the microhardness of the samples. Photoconductivity studies have been carried out using a photoconductivity set-up with a Keithley 485 picoammeter at room temperature.

III. RESULTS AND DISCUSSIONS

A. Solubility Measurement

Solubility is a measure of the chemical potential of solid in the saturated solution. The growth rate of a crystal depends on its solubility and temperature. Solvent and solubility factor define supersaturation which is the driving force for the rate of crystal growth. Hence for a material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion. The solubility of the samples was determined at different temperatures such as 30, 35, 40, 45, 50, 60°C. A constant volume of 50 ml of the saturated solution was used in this experiment. The measurement was performed by dissolving the sample in water in an airtight container maintained at a constant temperature with continuous stirring. The solution was constantly stirred for 2 h using magnetic stirrer for homogenization. Then solubility was determined by gravimetric method and the variation of solubility with the temperature for the grown crystals is presented in the figure 2. The results indicate that the solubility increases with increase of temperature for the samples. It is observed that when cesium chloride and rubidium chloride were added as the dopants, the solubility increases which indicates that the solvent is able to accommodate an increased amount of solutes for the saturation at the same temperature for samples.

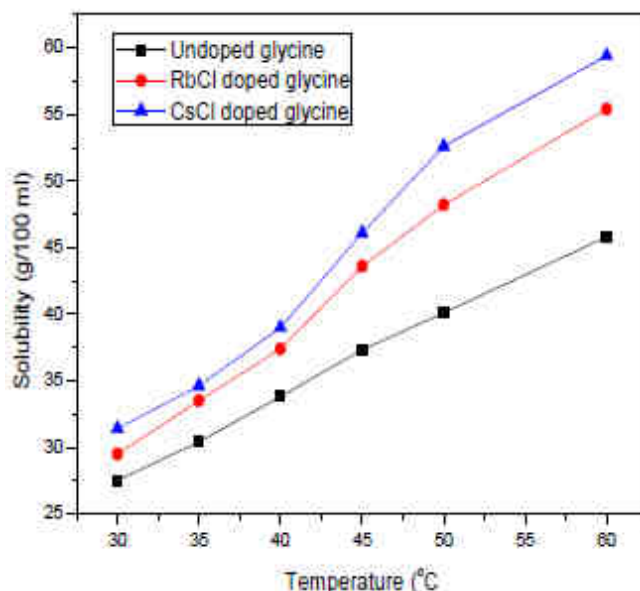


Fig.2: Solubility curves for undoped glycine, cesium chloride doped glycine and rubidium chloride doped glycine crystals

B. Nucleation kinetic studies

Nucleation kinetic studies are necessary to get the optimized growth parameters and these parameters can be used to grow good quality crystals by slow evaporation and slow cooling techniques. Initially the induction period was measured at different values of supersaturation ratio for the samples and using these values the critical nucleation parameters were determined. The time interval in which the first sparkling particle is formed in the supersaturated solution is called as the induction period. The induction period was measured by isothermal method at room temperature (30°C) at different supersaturation ratios (S) viz. 1.2, 1.25, 1.3, 1.35 and 1.4. A constant temperature bath, hot plate magnetic stirrer and a nucleation cell (corning glass beaker) were used for measuring the induction period. A powerful lamp was also used for observing the formation of the nucleation in the supersaturated solution. Supersaturated aqueous solution of the sample was taken in the nucleation cell and when the nucleation occurs in the cell, it grows quickly and a bright sparkling particle forms in the nucleation cell and time interval in which the first sparkling particle is formed in the solution was measured as the induction period. This procedure was followed for measuring the values of induction period at the different supersaturation ratios. The variations of induction period with supersaturation ratio for the samples are provided in the figure 3. The results show that the induction period decreases with supersaturation ratio for all the three samples. When rubidium chloride and cesium chloride were added as the dopants into glycine, the induction period is noticed to be decreasing. The classical homogeneous nucleation theory was adopted to determine the critical nucleation parameters and the formulae used for calculating the critical nucleation parameters are given in the reference [18]. The obtained values of Gibbs free energy change, critical radius, number of molecules in the critical nucleus and nucleation rate are given in the tables 1-3.

The critical parameters such as Gibbs free energy change, critical radius, number of molecules in the critical nucleus are observed to be decreasing with increase of supersaturation ratio and the nucleation rate decreases with increase of supersaturation ratio. The supersaturation and presence of impurities in the solution have an important role in controlling the nucleation rate, nucleation parameters and growth rate during the growth of crystals. The nucleation rate and growth rate of crystal depend on many factors like temperature, the degree of supersaturation of the solution, pH of the solution, concentration of the impurities in the solution, nature of the dopants, etc. [19].

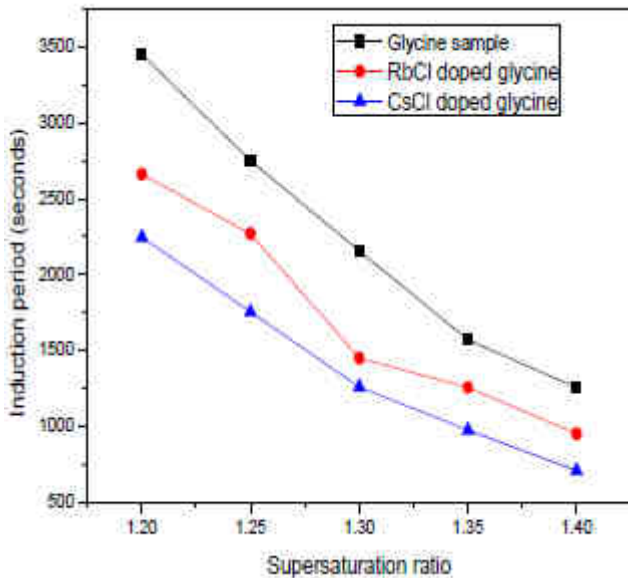


Fig. 3: Variation of induction period with supersaturation ratio for glycine, rubidium chloride (RbCl) doped glycine and cesium chloride (CsCl) doped glycine crystals

Table 1: Values of critical nucleation parameters for undoped glycine sample

S	$\Delta G^* \times 10^{-20}$ (joules)	$r^* \times 10^{-10}$ (m)	n	$J \times 10^{24}$ nuclei/s/volume	$\sigma \times 10^{-3}$ J/m ²
1.2	0.844	1.240	45	3.242	1.731
1.25	0.721	1.045	34	4.320	
1.3	0.595	0.874	27	6.034	
1.35	0.350	0.702	21	7.940	
1.4	0.236	0.636	17	8.236	

Table 2: Values of critical nucleation parameters for rubidium chloride doped glycine

S	$\Delta G^* \times 10^{-20}$ (joules)	$r^* \times 10^{-10}$ (m)	n	$J \times 10^{24}$ nuclei/s/volume	$\sigma \times 10^{-3}$ J/m ²
1.2	0.647	0.978	33	4.210	1.320
1.25	0.530	0.783	26	5.012	
1.3	0.378	0.540	20	7.231	
1.35	0.275	0.482	15	8.156	
1.4	0.178	0.304	13	9.120	

Table 3: Values of critical nucleation parameters for cesium chloride doped glycine

S	$\Delta G^* \times 10^{-20}$ (joules)	$r^* \times 10^{-10}$ (m)	n	$J \times 10^{24}$ nuclei/s/volume	$\sigma \times 10^{-3}$ J/m ²
1.2	0.511	0.698	25	6.344	1.038
1.25		0.534	18		
1.3	0.402	0.410	13		
1.35	0.270	0.303	10		
1.4	0.158	0.279	7		
	0.137			7.346	
				8.580	
				9.023	
				9.891	

C. Structural parameters

The grown crystals cesium chloride doped glycine and rubidium chloride doped glycine were subjected to single crystal XRD studies to obtain the crystal structure and the lattice parameters. A single crystal X-Ray Diffractometer (Bruker-Nonius MACH3/CAD4) was used to obtain the single crystal XRD data of the grown crystals and the data are given in the table 4. The crystal structure of cesium chloride doped glycine and rubidium chloride doped glycine crystals are found to be monoclinic structure. The values of lattice parameters for undoped glycine crystal were obtained by Richard E.Marsh and for the comparative purpose, these values are given in table 4. The obtained values of structural parameters for cesium chloride doped glycine and rubidium chloride doped glycine crystals are given in the table 4. From the results, it is observed that the crystal cell parameters are slightly altered when glycine crystals are doped with cesium chloride or rubidium chloride.

Table 4: Values of lattice parameters for cesium chloride doped glycine crystal and rubidium chloride doped glycine crystal

Sample	Unit cell parameters
Undoped glycine crystal	a = 5.102 Å , b = 11.9709 Å , c = 5.4575 Å , [20] $\alpha = 90^\circ, \beta = 111.42^\circ, \gamma = 90^\circ, V = 310.30 (\text{Å})^3$
Cesium chloride doped glycine crystal	a = 5.113(5) Å , b = 11.987(4) Å , c = 5.446(6) Å , $\alpha = 90^\circ, \beta = 111.51^\circ, \gamma = 90^\circ, V = 311.02 (2) (\text{Å})^3$



Rubidium chloride doped glycine crystal	$a = 5.108(6) \text{ \AA}$, $b = 11.962(5) \text{ \AA}$, $c = 5.490(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 112.07^\circ$, $\gamma = 90^\circ$, $V = 310.87(3) (\text{ \AA})^3$
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D. Measurement of density of the grown crystals

The floatation technique was used to find the crystal density and this method is sensitive to point defects and insensitive to dislocations unlike other methods. An important feature of this method is that only a small amount of substance is required for the measurement density. The solvents used for finding the density of crystals here are carbon tetrachloride and bromoform. An electronic balance and a specific gravity bottle were used in this experiment. The calculated values of density of sample crystals are provided in the table 5. It is observed from the results that the density values slightly increase when dopants like cesium chloride or rubidium chloride were added into glycine crystals.

Table 5: Values of density of the samples

Sample	Density (g/cc)
Undoped glycine crystal	1.608
RbCl doped glycine	1.672
CsCl doped glycine	1.687

E. Measurement of SHG

The powder technique of Kurtz and Perry [21] with a pulsed Nd:YAG laser was used to measure the second harmonic generation (SHG) efficiency. The grown crystals were ground to powder of grain size 400-800 μm and subjected to measurement of SHG. From this technique, it is noticed that there is no emission of green radiation from the samples when infrared laser light of 1064 nm is passed onto the powder samples. This test shows that the grown undoped and doped samples crystallize in a centrosymmetric space group and hence the samples do not show second order NLO behaviour.

F. Microhardness studies

Microhardness measurements were performed using a Vickers microhardness tester. In the present work, undoped, cesium chloride doped and rubidium chloride doped glycine crystals were subjected to microhardness test for different loads and indentation time given was 10 s. For each load, several indentations were made and the average diagonal length (d) was measured. Microhardness number 'H_v' was determined using the relation $H_v = 1.8544 P/d^2 \text{ kg mm}^{-2}$ where P is the load applied in kg and d is the diagonal length of the indented impressions in mm. Plots between hardness values and the corresponding loads for the sample crystals are drawn and are presented in the figure 4. From the results of microhardness studies, it is observed that hardness number (H_v) increases with load for all the grown crystals. This can be explained on the basis of depth of penetration of the indenter. When the load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in the load. The measured hardness is the characteristics of these layers and

the increase in the hardness number is due to the overall effect on the surface and inner layers of the sample and hence this is due to reverse indentation size effect. Hardness is found to be increasing when cesium chloride or rubidium chloride are added as dopants into the lattices of glycine crystals. The addition of dopants into glycine crystals most probably enhances the strength of bonding with the host material and hence hardness increases. These impurity defects in the lattices of glycine crystals may act as obstacles to dislocation motion and thus increasing the hardness of the crystals [22]. The relationship between load(P) and diagonal length (d) of indentation is given by $P = a d^n$. This is called as Meyer's law. Here a and n are constants for a particular material. From the straight line graph of log P versus log d, the slope can be obtained. The slope is equal to the constant n which is called as Mayer's index number or work hardening coefficient. Plots of log P versus log d for the samples are displayed in the figure 5. The obtained values of work hardening coefficient are 2.752, 2.657 and 2.435 respectively for undoped, cesium chloride doped and rubidium chloride doped glycine crystals. Since these values are more than 1.6, the grown samples belong to the soft material category.

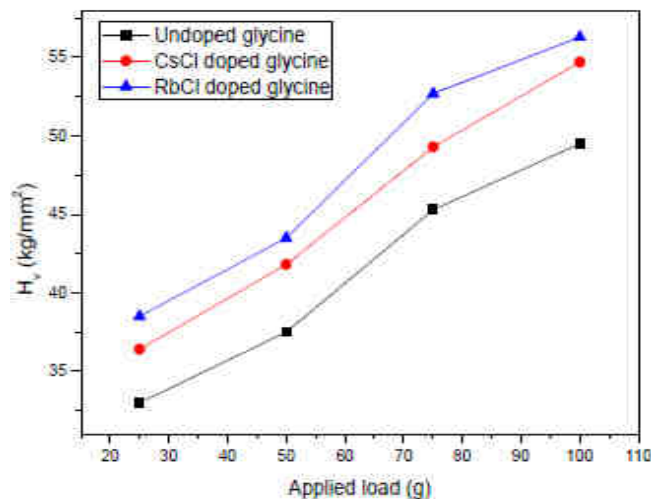


Fig.4: Plots of microhardness number versus the applied load for undoped, cesium chloride doped and rubidium chloride doped glycine crystals

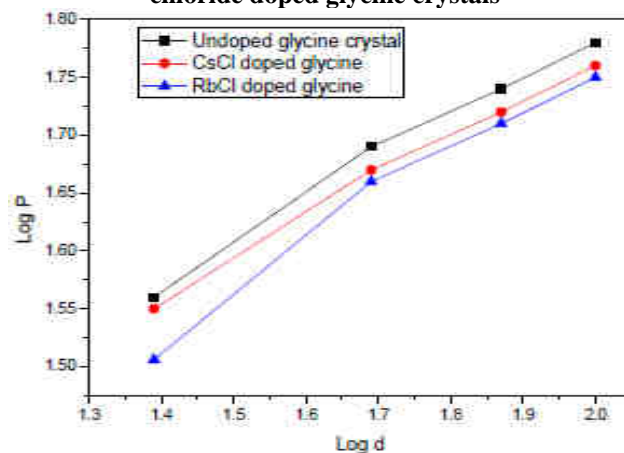


Fig.5: Plots of log P versus log d for undoped, cesium chloride doped and rubidium chloride doped glycine crystals



G. Photoconductivity studies

The photoconductivity studies for the grown crystals were carried out by measuring dark and photo currents at different applied electric fields. 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 at a spacing of about 0.9 mm on the samples using silver paint. Increasing the DC voltage, the corresponding values of dark current was noted from the electrometer. In order to measure the photo current, the sample was illuminated with a halogen lamp (100 W) by focusing a spot of light on the sample with the help of a convex lens. The DC input was increased in the same range as done in the previous case and the corresponding photocurrents were measured. The variations of dark and photo currents for undoped, cesium chloride doped and rubidium chloride doped glycine crystals with the applied loads are presented in the figure 6. It is noticed that the values of dark current and photo current increase with increase of applied electric field. For all 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[23].

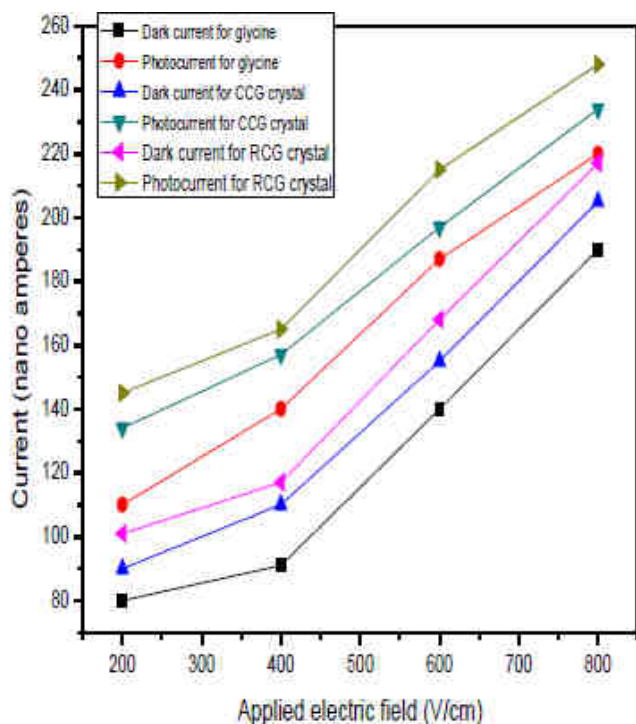


Fig.6: Plots of photocurrent and dark current versus the applied field for undoped, cesium chloride doped glycine (CCG) and rubidium chloride doped glycine(RCG) crystals

IV. CONCLUSIONS

The single crystals such as undoped glycine, cesium chloride doped glycine and rubidium chloride doped glycine were grown by solution method. Solubility values are observed to be more when glycine crystals are doped with cesium chloride or rubidium chloride. Critical nucleation parameters were determined by isothermal technique. The lattice parameters for the grown crystals were found by single crystal XRD studies. Density values are found to be more for

the doped glycine crystals. From hardness studies, it is proved that the grown crystals belong to soft type of materials. Photoconductivity studies reveal that the grown crystals are the positive type of photoconductors. SHG studies are used to confirm that the grown crystals like undoped glycine, cesium chloride doped glycine and rubidium chloride doped glycine samples are centrosymmetric crystals.

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