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Studies on growth and Characterization of urea-doped diglycine picrate (DGP) single crystals

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Abstract
Urea-doped diglycine picrate (DGP) single crystals were grown by solution method with slow evaporation technique. The solubility of the urea-doped DGP was carried out at various temperatures and it is observed that the solubility of urea-doped DGP is higher than that of pure DGP crystal. When urea was added as dopant, morphological alterations were noticed in DGP crystal. Cell parameter values of the grown urea-doped DGP crystal were obtained from the XRD analysis and the presence of functional groups was identified from FTIR study. Dlectric studies were performed for the grown crystals and it is found that the values of dielectric constant and loss for urea-doped DGP crystal are more than those of pure DGP crystal. The Vickers microhardness values were measured for the grown crystals. From the microhardness study, it is observed that urea- doped DGP crystal is harder than pure DGP crystal.

Keywords: Diglycine picrate; solubility; Crystal growth; Characterization; FTIR; XRD; microhrdness; dielectric constant

INTRODUCTION

In recent times, organic Nonlinear Optical (NLO) crystals have attracted considerable attention because they have often large NLO coefficient compared to inorganic crystals. The organic NLO crystals provide the key functions of optical frequency doubling, optical modulation, optical switching and optical memory for emerging photonic technologies [1-3]. Glycine, the simplest organic material, exhibits in six distinct polymorphic forms viz. ▯-glycine, ▯-glycine and ▯-glycine at ambient temperature and pressure and δ, ε and β’-forms under high pressure. It combines with organic and inorganic salts and acids to form interesting NLO materials. Picric acid is used to form interesting NLO picrates when it combines with other organic and amino acids [4-6]. The crystal structure for glycine picrate was determined by Kai et al [7]. Glycine picrate was first obtained by Levene et al [8] and it was concluded that the crystal has 1:1 composition. However, it was corrected by the same author [9] to point out that the crystal structure obtained by Kai et al was in reality for diglycine picrate and not for glycine picrate. Diglycine picrate crystal belongs to monoclinic crystal system and it is reported to be a useful NLO material [10-12]. Doping NLO crystals with organic impurities can alter various physical and chemical properties and doped NLO crystals may find wide applications in optoelectronic devices compared to pure NLO crystals [13-15]. Though numerous experimental data concerning the influence of impurities on crystal growth are available yet the influence of urea doping and its concentration in organic single crystals needs thorough investigation. Hence in this paper, we report the results of our work on the growth of urea-doped diglycine picrate crystals by slow evaporation method along with the characterization by X-ray diffraction (XRD), fourier transform infrared (FTIR), UV visible transmittance studies, dielectric and microhardness techniques.

EXPERIMENTAL

Commercially available Analar Reagent (AR) grade of glycine and picric acid in the molar ratio of 2:1 were used for synthesis of diglycine picrate. The calculated amounts of glycine and picric acid were dissolved in de-ionized water and stirred well using a magnetic stirrer for about 3 hours. The solution was heated until the synthesized salt of pure diglycine picrate was obtained. 1 mol % of urea was added to the solution of diglycine picrate to obtain urea-doped diglycine picrate salt . The pure and urea-doped diglycine picrate salts were re-crystalaized several times to improve purity. Solubility study for the synthesized salts was carried out using a hot-plate magnetic stirrer and a digital thermometer. By adjusting the voltage regulator in the hot plate magnetic stirrer, the temperature was maintained at 30 °C initially. The synthesized salt was added step by step to 50 ml of de-ionized water in an air-tight container kept on the hot-plate magnetic stirrer and stirring was continued till a small precipitate was formed. This gave confirmation of supersaturated condition of the solution. Then, 25 ml of the solution was pipetted out and taken in a petri dish and it was warmed up at 45 °C till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of diglycine picrate salt in de-ionized water was determined gravimetrically [16,17]. The same procedure was followed to find solubility of pure and urea-doped diglcine picrate samples at various temperatures. The variation of solubility with temperature for the samples is presented

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in 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 urea-doped diglylcine picrate sample. It is clear that for the urea-doped sample, the solvent is able to accommodate a marginally increased amount of solute for the saturation at the same temperature. Since solubility increases with temperature, the samples of this work have positive temperature coefficient of solubility. The increase in solubility for the urea-doped sample may lead to change of thermodynamic parameters such as surface concentration of growth species and the surface energy and hence it may be responsible for the change in the growth rate, morphological change during growth of crystals. Saturated solutions were prepared using the solubility data and the seed crystals were obtained in a period of 7 days using slow evaporation method. Bulk crystals of pure and urea-doped diglycine picrate were grown from the saturated solutions of corresponding synthesized salts using submerged seed solution evaporation technique.

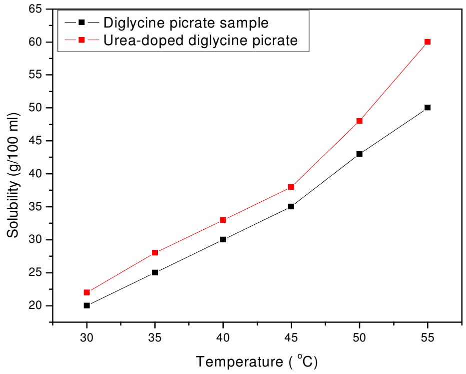

Fig 1. Variation of solubility with temperature for pure and urea-doped diglycine picrate samples.

Analyzing techniques

In order to find the lattice parameters of the grown crystals, single crystal X – ray diffraction studies have been carried out using Enraf Nonius CAD4 diffractometer with Mo Kα(λ= 0.7170 Å). Powder X-ray diffraction patterns of the samples were obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu Kα radiations (λ= 1.54056 Å) at 35 kV, 10 mA). The samples were scanned over the required range for 2 theta values (5 – 70 °). The crystalline phase of the samples was identified from the crystallographic parameters such as two theta, relative intensity and hkl values. The FTIR spectra of sample crystals have been recorded on a SHIMADZU spectrometer using KBr pellet method in the range 400 – 4000 cm^{-1} to reveal the functional groups. Microhardness hardness study of the grown crystals was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Indentations were made for various loads and 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. Measurements of dielectric parameters like dielectric constant(ε_r) and dielectric loss (tan δ) of crystals were carried out using an LCR meter (Agilent 4284A) at various frequencies in the range 10^2 - 10^6 Hz

RESULTS AND DISCUSSION

XRD studies

Single crystal XRD and powder XRD studies for the grown crystals were carried out and the collected data are provided in the table 1. From the data, it is observed that the grown crystals crystallize in monoclinic system. The slight changes of lattice parameters have been noticed for the urea-doped sample compared to pure diglycine picrate crystal. The changes in the lattice parameters are due to incorporation of urea in the lattice of diglycine picrate crystal. The powder X-ray diffraction (XRD) pattern urea- doped diglycine picrate crystal are shown in the figure 2. The well-defined peaks at specific 2Θ values show high crystallinity of the grown crystals. All the reflections of powder XRD patterns of this work were indexed using the TREOR software package following the procedure of Lipson and Steeple [18]. The values of hkl, relative intensity and 2 theta values for the reflection peaks of the powder XRD pattern are given table 2.

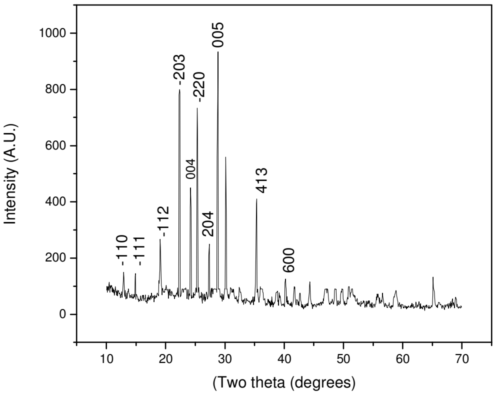

Fig 2.Powder XRD pattern for urea-doped diglycine picrate sample

Table 1.Single crystal XRD data for undoped and urea-doped diglycine picrate crystals

Sample	Cell parameters	Volume (Å)^3	Z
Undoped Diglycine picrate crystal	a= 14.894 (1) Å b=6.870(2) Å c= 15.154(2) Å α = 90 °, β= 93° γ=90°	1548.45	2
1 mol % of urea-added diglycine picrate crystal	a= 14.454(1) Å b=7.176(1) Å c= 15.054(2) Å α = 90 °, β= 88 ° γ=90°	1560.47	2

Table 2. Values of 2 theta, relative intensity and hkl for urea-doped diglycine picrate sample

Peak No.	2 theta (degrees)	Relative intensity (%)	hkl
1.	13.64	10	-1 1 0
2.	14.94	9	-1 1 1
3.	18.85	25	-1 1 2
4.	22.34	84	-2 0 3
5.	24.23	43	0 0 4
6.	25.31	71	-2 2 0
7.	27.34	18	2 0 4
8.	29.98	100	0 0 5
9.	35.54	37	4 1 3
10.	40.28	11	6 0 0

FTIR analysis

The Fourier Transform Infrared (FTIR) Spectrum was recorded for the sample in the range of 400-4000 cm^{-1} following the KBr pellet technique and it is shown in figure 3. The assignments for the absorption peaks/bands in the spectrum are given using the available IR spectral data and the corresponding vibrational group assignments are given in the table 3. It is to be mentioned here that the FTIR spectrum for pure (undoped) diglycine picrate sample is not presented because it is very similar to that of urea-doped diglycine picrate sample.

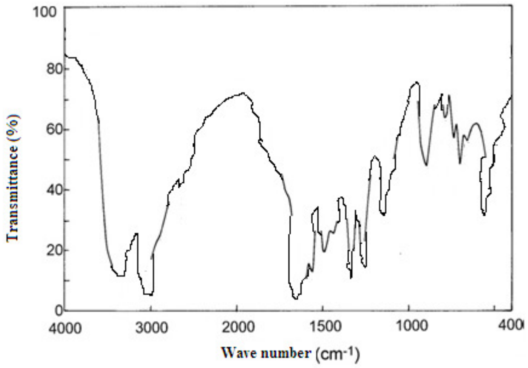

Fig 3.FTIR spectrum of urea-doped diglycine picrate sample

Table 3: FTIR spectral assignments for urea-doped diglycine picrate sample

Wave number (cm^{-1})	Assignments
3390	OH stretching
3082	NH_3^+ symmetrical stretching
1710	C=O stretching
1560	deformation of NH_3^+
1420	COO^- stretching
1330	NO_2 stretching
1272	OH deformation
1155	Phenolic O
790	C-C skeletal stretching
701	N-H bending
525	NO_2 scissoring

Measurement of hardness

Hardness is a measure of materials resistance to localized plastic deformation. The microhardness characterization is extremely important as far as the device fabrication is concerned. The selected smooth surfaces of the grown crystals were used for microhardness measurement at room temperature using a Vickers microhardness tester fitted with a diamond indenter. The hardness of the crystal is calculated using the relation The hardness of the crystal is calculated using the relation.

$$H_v = 1.8544\ P / d^2 \qquad kg / mm^2$$

where P is the applied load in kg and d is the length of indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid [19]. A plot of the hardness number and the load is depicted in figure 4. It is noticed that Vickers hardness number (H_v) increases with the applied load satisfying the indentation size effect. When a DGP crystal is doped with urea, the hardness increases and this increase in the hardness value of doped sample can be attributed to the incorporation of urea in the lattice of the host crystal.

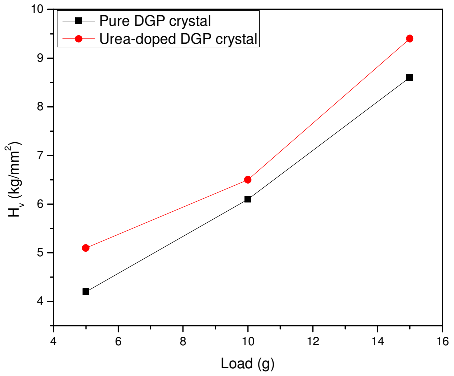

Fig 4. Variation of microhardness number with load for pure and urea-doped diglycine picrate crystals

Measurement of dielectric constant and dielectric loss

The measurement of dielectric constant (ε_r) and loss ($\tan\delta$) as a function of frequency and temperature gives the ideas of electrical processes that are taking place in materials and these parameters were measured for the samples of this work. Dependence of dielectric constant and dielectric loss of pure and urea-doped diglycine picrate crystals as a function log frequency [log(f)] at temperature 35 °C are displayed in the figures 5 and 6. Since frequency values vary from 10^2 - 10^6 Hz, the scale will not be equal if log frequency is not taken along X-axis of the figures 5 and 6. The obtained results suggest that the dielectric constant and loss strongly depend on the frequency of applied field. It is observed from the results that both dielectric constant and loss are high at low frequencies and they decrease with increase in frequency and attain almost constant values beyond 10^4 Hz. It is noticed that the values of ε_r and $\tan\delta$ are more for urea-doped glycine picrate crystal when compared to that of undoped glycine picrate sample. The values of dielectric constant and loss are high at low frequencies and decreases at higher frequencies. This may be due to the fact that at lower frequencies space chage polarization is active and at higher frequencies the ionic and electronic polarizations are active [20].

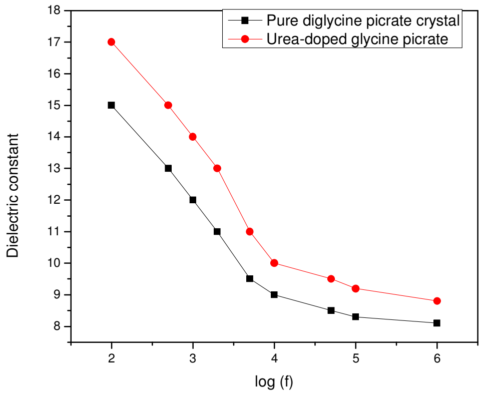

Fig 5. Variation of dielectric constant as a function of frequency for pure and urea-doped diglycine picrate crystals

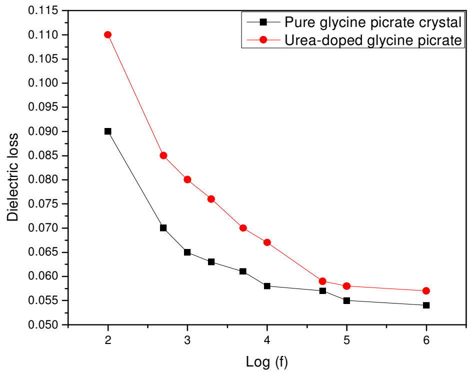

Fig 6. Variation of dielectric loss as a function of frequency for pure and urea-doped diglycine picrate crystals

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