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RESEARCH ARTICLE

INFLUENCE OF ZINC CHLORIDE ON THE STRUCTURAL, OPTICAL, MECHANICAL AND NLO PROPERTIES OF DIGLYCINE PICRATE (DGP) SINGLE CRYSTAL

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ABSTRACT

Diglycine Picrate (DGP) and zinc chloride doped DGP crystals were grown by solution growth method using slow evaporation technique. EDS spectrum of the doped crystals are taken to confirm the presence of the dopants. The lattice parameters are obtained through single crystal XRD study. The powder XRD spectrum helps to prove the crystalline nature of the crystal and also to identify planes present in the crystals. The UV-Vis-NIR study reveals the optical property of the grown crystals. The hardness behavior of the crystals is analyzed by using Vickers microhardness test. The NLO efficiency of the grown crystals was measured through powder Kurtz and Perry technique.

INTRODUCTION

In the past two decades, Nonlinear Optical (NLO) crystals have attracted the scientists and technologists due to their potential applications in the area of photonics. 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]. Picric acid forms interesting NLO picrates when it combines with organic and amino acids due to the presence of active π- and ionic bonds [4]. Glycine picrate is an organic material that belongs to triclinic crystal system. Normally, non-centrosymmetric crystals exhibit NLO property. However, very few crystals are found to have NLO property even though they crystallize in centrosymmetric form and glycine picrate belongs to this category. Organic NLO materials are often formed by weak Van der Wall's and hydrogen bonds and hence possess high degree of delocalization. Glycine picrate crystal was first grown by Levene et al. [5]. Later on, Kai et al. [6] resolved the structure of glycine picrate crystal and reported that the crystal consists of two molecules of glycine and one picric acid molecule and is formed through hydrogen bonding. The hydrogen atom of phenolic hydroxyl group of picric acid migrates from picric acid to glycine and hence a single hydrogen atom is shared by carboxylic group of two glycine molecules. Shakir et al. [7] have grown the crystal from aqueous solution containing glycine and picric acid at 1:1 molecular ratio but, it was found that the obtained mono crystals are really diglycine picrate and not glycine picrate. Thilagavathy et al. [8] have grown Diglycine Picrate (DGP) crystal using unidirectional growth technique owing to its greater advantages like high solute-solid conversion, minimum thermal stresses on the crystal during growth and prevention of microbial growth. Uma Devi et al. [9] have reported on the dielectric and Z-scan measurements of DGP crystal. Doping NLO crystals with organic or inorganic impurities can alter various physical and chemical properties and doped NLO crystals find wide applications in opto electronic devices compared to pure NLO crystals because of their enhanced qualities. Balasundari *et al.* [10] have grown urea doped DGP crystals and reported on the optical and hardness behavior of the crystal. Rajarajan et al. [11] have doped glycine picrate crystal with $CuCl_2$ and carried out its structural characterization studies. In the present work, an effort was made to grow diglycine picrate (DGP) doped with zinc chloride for the first time. For this purpose, DGP crystal was doped with $ZnCl_2$ in

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three different concentrations, namely, 5, 10 and 15 weight percentages. Only 5 and 15 wt. % doped solutions yielded quality crystals whereas the 10 wt. % doped solution leads to poly crystals. Hence, the growth and characterization of pure DGP, 5 and 15 wt. % zinc chloride doped DGP crystals are reported.

EXPERIMENTAL METHODS

Synthesis

Synthesized salt of pure DGP was prepared by dissolving glycine and picric acid taken in 2:1 ratio in de-ionized water. The solution was stirred well using magnetic stirrer for 2 hours at 30^{o} C. The solution was taken in a petri dish and heated. The complete evaporation of the solvent left behind the synthesized salts. In order to synthesize the $ZnCl_2$ doped DGP sample, the dopant was added in 5 and 15 wt. % to the diglycine picrate solution in separate beakers and the same procedure was repeated.

Solubility

Solubility is the amount of salt (in gram) present in 100 ml of solvent. In solution growth technique, the size of a crystal depends on the amount of the material available in the solution which in turn is decided by the solubility of the material in that solvent. The solubility test of pure and zinc chloride doped DGP salts were carried out at different temperature by gravimetric method [12]. The solubility curves are drawn for the three samples as shown in Fig.1.

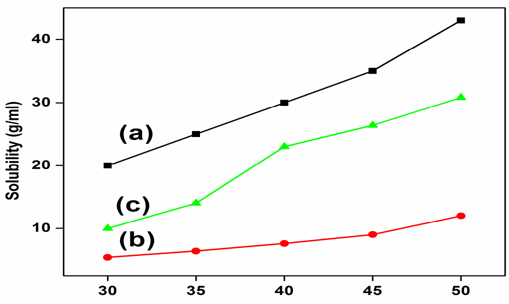
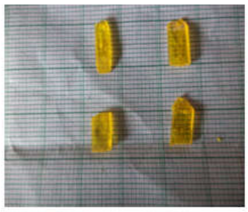


Fig.1 Solubility curves of (a) pure DGP, (b) 5 wt. % and (c) 15 wt. %zinc chloride doped DGP crystals

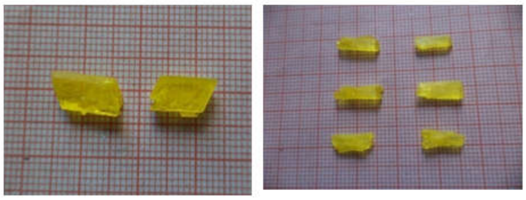
From the results, it is observed that the doped crystals have less solubility than the pure DGP crystals. Thus, the dopant $ZnCl_2$ inhibits the solubility. Anantha Babu et al. [13] have reported that impurity absorption on any crystal leads to two opposing effects: (i) the impurity lowers the surface tension and leads to higher growth rate and (ii) the impurity blocks potential growth sites leading to lower nucleation rates. Also, it is observed from the figure that the solubility of the grown crystals is found to increase with temperature. The positive temperature coefficient of the curves ensures that slow evaporation technique is the suitable method to grow these crystals.

Crystal growth

Saturated solutions of pure DGP and the zinc chloride doped DGP salts were prepared in separate beakers by dissolving their synthesized salts in de-ionized water. Each solution was stirred for 2 hours using magnetic stirrer at 35^{o}C for homogeneous mixing. The solutions were filtered using Whatmann filter papers and the beakers containing the solutions were covered with perforated sheets. Big sized crystals were harvested from these solutions by slow evaporation method in a span of 15 days. The crystals are yellow in colour and they remain stable under standard conditions. The grown crystals are shown in Fig.2.



(a)



(b) (c)

Fig.2 Photographs of (a) pure DGP, (b) 5 wt. % and (c) 15 wt. % zinc chloride doped DGP crystals

RESULTS AND DISCUSSION

EDS analysis

The diffusion of dopant into the crystals can be confirmed through Energy Dispersive X-ray (EDS) studies. EDS spectra of the doped crystals are taken using JEOL model JED-2300 instrument and are shown in Fig.3. The figures prove that the metal ion Zn has entered into the host DGP crystal.

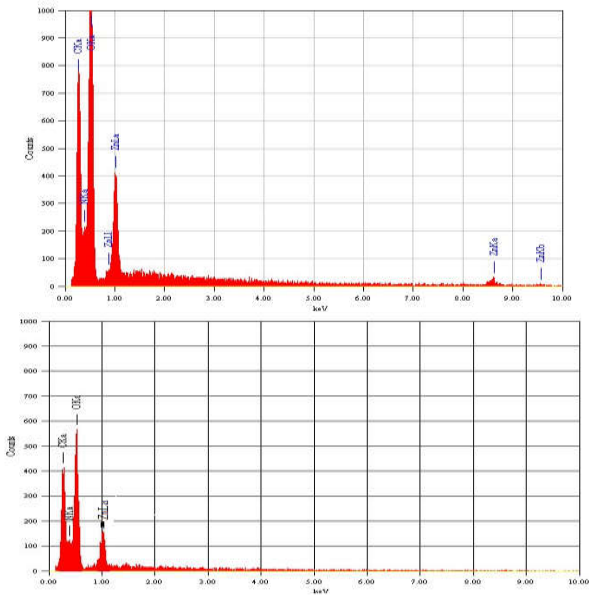


Fig.3 EDS spectrum of (a) 5 wt. % and (b) 15 wt. % Zinc chloride doped DGP crystals

X-ray Diffraction

X-ray diffraction helps to determine the arrangement of atoms and hence to determine the lattice parameters of crystalline material. The lattice parameters of pure and zinc chloride doped DGP crystals are determined by single crystal XRD study using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK$_\alpha$ radiation and are listed in Table 1. The pure and ZnCl2 doped DGP crystals are found to be monoclinic in structure. As the concentration of the dopant is changed, slight variation in the lattice parameters is observed.

Table 1 Lattice parameters of pure and zinc chloride doped DGP crystals

Lattice parameters	pure DGP	zinc chloride doped DGP	
		5 wt. %	15 wt. %
a (Å)	14.368(3)	14.297(1)	14.353(5)
b(Å)	7.822(2)	7.923(4)	7.966(9)
c (Å)	15.165(3)	14.978(1)	14.955(23)
α	90°	90°	90°
β	93.65°	91.91(4)°	91.78(13)°
γ	90°	90°	90°

Powder X-ray diffraction patterns of the samples are taken using a powder X-ray diffractometer, PAN alytical model, Nickel filtered CuK$_\alpha$ radiation at room temperature. The powder XRD spectra of pure and zinc chloride doped DGP crystals are displayed in Fig.4. The sharp well-defined peaks show the crystalline nature of the grown crystals. The appearance of new peaks and the intensity variations observed in the XRD spectrum of doped crystals prove the incorporation of the dopant into the host crystal.

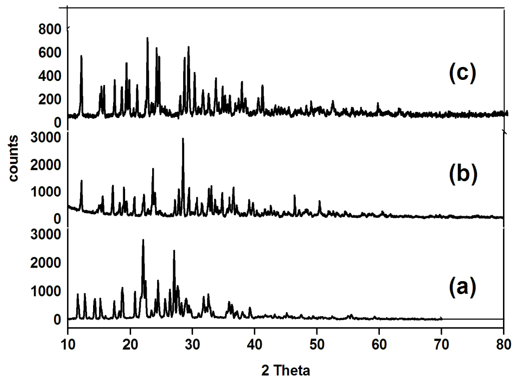


Fig.4 Powder XRD spectra of (a) pure DGP, (b) 5 wt. % and (c) 15 wt. % zinc chloride doped DGP crystals

UV-Visible-NIR spectral study

To determine the transmission range and hence to know the suitability of the grown crystals for optical applications, the UV spectra are recorded using Lambda 35 spectrometer in the optical range of 190-1100 nm by using crystals of thickness 2 mm and they are shown in Fig.5. The transmittance spectrua of grown crystals show the same cut-off wavelength of 324 nm. The lower cut-off wavelength and the observance of no absorption peak in the visible and IR regions are the characteristics of amino acid. The absorption band appearing in the UV-Vis region may be due to the coloured nature of the material [9].This also signifies that the grown crystals are transparent to green light which is the essential property for SHG material [7]. The grown crystals are quite transparent in the wavelength region 600-1100 nm which may be due to electronic transitions associated with the carboxylate anion and the nitryl cation bonds [14]. The pure DGP crystal exhibits a transmittance of 40 % and 5 wt. % zinc chloride doped crystal has higher transmittance compared to 15 wt. % doped crystal.

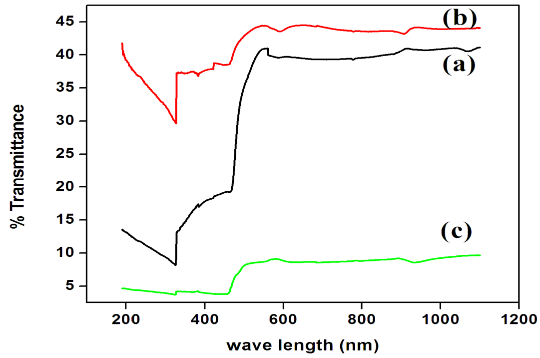


Fig.5 Transmittance spectra of (a) pure DGP, (b) 5 wt. % and (c) 15 wt. % zinc chloride doped DGP crystals

Microhardness Test

Hardness is the resistance offered by a solid to the movement of dislocation. The Vickers microhardness values of the grown crystals are calculated using the relation $H_v = 1.8544\ P/d^2$ kg/mm^2 where P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramidal indenter [16]. A plot of the hardness number and the applied load is depicted in Fig.6. From the graph, it is seen that the hardness value of 5 wt. % zinc chloride doped DGP crystal is greater than that of pure DGP crystal. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of indentation. Higher hardness value indicates that greater stress is required to produce dislocations thus confirming greater crystalline perfections [17]. But, the 15 wt. % zinc chloride doped crystal has low hardness value which may be due to the development of more number of microcracks around the indentation mark [18]. The observed hardness results are in accordance with the fact that the quality of the crystal is enhanced only for low concentration of the dopant. The grown crystals show Reverse Indentation Size Effect (RISE) in which the hardness value increases with increase of load [19].

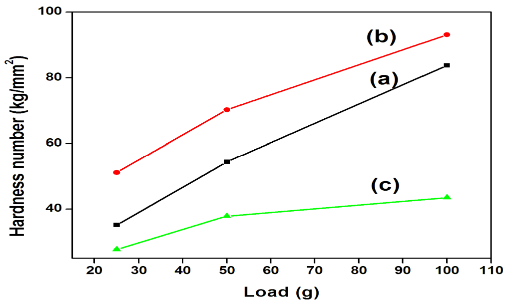


Fig.6 Hardness value of (a) pure DGP, (b) 5 wt. % and(c) 15 wt. % zinc chloride doped DGP crystals

The yield strength (σ_y) of the material which is a measure of minimum stress required to resist permanent deformation and it is calculated 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 [22,23] and the values are given in the table 2. From results, it is observed that yield strength and stiffness constant of samples increase with increase of the applied load.

Table 2 Values of yield strength and stiffness constant of grown crystals

Load (grams)	Pure DGP		5 wt. % $ZnCl_2$ doped DGP		15 wt. % $ZnCl_2$ doped DGP	
	σ_y (MPa)	C_{11} (10^{14} Pa)	σ_y (MPa)	C_{11} (10^{14} Pa)	σ_y (MPa)	C_{11} (10^{14} Pa)
25	114.66000	1.5686	167.0064	3.029183	90.32333	1.03322
50	177.54333	3.37152	229.5898	5.287005	123.4800	1.78582
100	273.58333	7.18538	304.0951	8.645879	141.6100	2.27881

SHG Measurement

The first and the most widely used technique for confirming the SHG efficiency of NLO materials is the Kurtz powder technique [24]. The SHG efficiency is determined for pure DGP and zinc chloride doped DGP crystals using a Nd:YAG, 10 ns laser with a pulse repetition rate of 10 Hz working at 1064 nm. The samples are ground into fine powder and tightly packed in different micro-capillary tubes. The samples are mounted one by one in the path of laser beam of 0.68J pulse energy. KDP sample ground into identical size is used as reference material in the SHG measurement. SHG conversion efficiency is computed by the ratio of signal amplitude of the grown crystals to that of the KDP signal amplitude recorded for the same input power. The efficiency of pure DGP, 5 and 15 wt. % zinc chloride doped crystals are found to be 1.117, 0.77 and 0.53 times that of KDP respectively.

CONCLUSION

Crystals of pure diglycine picrate (DGP), 5 wt. % and 15 wt. % zinc chloride doped diglycine picrate are grown by slow evaporation technique. Yellow coloured crystals were harvested after 15 days. The structural, optical and mechanical property of the grown crystals are analysed to know the effect of the dopant 'zinc chloride' on DGP crystals. The diffusion of the metal zinc into the crystal is confirmed by taking EDS spectra of the doped crystals. The structure of pure and doped DGP crystals is found to be monoclinic. The powder X-ray spectrum indicates the observance of new peaks and intensity variations of the peaks due to incorporation of dopant. The optical study reveals that 5 wt. % zinc chloride doped crystal has higher transmittance than pure DGP crystal. The hardness value of 5 wt. % zinc chloride doped DGP crystal is greater than that of pure DGP crystal. The NLO efficiency of the pure DGP, 5 and 15 wt. % zinc chloride doped crystals are found to be 1.117, 0.77 and 0.53 times that of KDP respectively. Finally, it is concluded that when zinc chloride is added in lower concentration, the quality of the crystal is enhanced.

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