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A STUDY ON THE GROWTH OF PURE AND ZINC SULPHATE MONO HYDRATE DOPED GLYCINE NLO SINGLE CRYSTALS AND THEIR PROPERTIES

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ABSTRACT

Single crystals of glycine, zinc sulphate monohydrate and zinc sulphate monohydrate doped glycine (ZSG) had been grown by slow evaporation technique at room temperature. The grown crystals had been subjected to different characterization studies to find its suitable applications. The crystalline nature of the grown compounds was confirmed by the powder X- ray diffraction (XRD) analysis. Single crystal XRD confirmed the structure of the doped crystal as monoclinic. UV-Vis transmittance study proved the enhancement of optical behaviour of the ZSG crystal. The FTIR spectrum had been recorded in the region 4000-400 cm^{-1} to identify the presence of functional groups. Thermo gravimetric analysis (TGA) helped to determine the upper limit of temperature up to which the grown crystals are thermally stable. The grown crystals were subjected to Vicker's Micro hardness analysis to ascertain their mechanical properties.

Key words: Single Crystal, XRD, Optical studies, FTIR, TGA, Micro hardness

INTRODUCTION

Second order non linear optical (NLO) materials have paid attention among crystal growers because of their potential applications in optoelectronic technologies. Such materials with large second order optical non linearity, short transparency cut-off wavelengths and stable physical and thermal performance are used in these emerging applications[1]. Inorganic materials have good mechanical and thermal properties with comparatively low optical non-linearity. The organic NLO materials have a large optical susceptibility, high optical thresholds for laser power and inherent ultrafast response times compared to inorganic materials. However, most of the organic NLO crystals are soft in

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nature, difficult to grow in large-sized single crystals and difficult to polish. Also they have low laser damage threshold. These materials have intense absorption in UV region, poor mechanical and thermal properties.

In view of these deficient properties, new type of hybrid NLO materials had been explored from organic-inorganic complexes with stronger ionic bond to improve their chemical stability, laser damage threshold, thermal and physical properties, and linear and nonlinear properties. Amino acids and their complexes belong to a family of organic materials[2-5]. Unlike other amino acids, glycine has no asymmetric carbon atom and is optically inactive. It has three crystalline forms (α, β and γ) of which α-glycine is commonly available[6]. Glycine and its methylated analogs form complexes with mineral acids exhibiting interesting ferroelectric behaviour[7]. Hence, to attain the desirable properties of organic and inorganic compounds, zinc sulphate is doped with glycine in this work. The present paper deals with the growth and characterization of zinc sulphate doped glycine (ZSG) single crystals along with its parent crystals.

EXPERIMENTAL

Materials and methods

In this work, $ZnSO_4.H_2O$ and glycine of 99.9% purity (AR grade) were used for the crystal preparation. Saturated solutions of $ZnSO_4.H_2O$ (57.7 g/100 mL) and glycine (24.99 g/100 mL) were prepared using doubly distilled water and filtered twice using Whatman No.1 filter paper to remove dust particles and undissolved materials. As another part of the solution, saturated solutions of $ZnSO_4.H_2O$ and glycine were mixed in the ratio 1:3 and stirred continuously using magnetic stirrer (REMI 1MLH) for six hrs. The saturated solutions of $ZnSO_4.H_2O$ of pH 5 and glycine of pH 5 and the mixture of the above two of pH 3 were taken in three separate beakers, covered with perforated aluminium foil and allowed for slow evaporation in a dust free and vibration free environment. Single crystals of $ZnSO_4.H_2O$, glycine and ZSG were grown from supersaturated solutions at room temperature. Periodic visual observation ensured the growth of crystals. Transparent, single crystals of $ZnSO_4.H_2O$, glycine and ZSG were harvested after a time span of 10, 14, and 61 days, respectively from the respective solutions. ZSG – the offspring of the following reaction:

$$ZnSO_4.H_2O + CH_2NH_2COOH \longrightarrow (NH_3+ - CH_2 - COO^-).ZnSO_4$$

The photographs of the harvested single crystals are shown in Fig. 1(a), (b), and (c), respectively. The dimensions of the grown single crystals were found to be 9 x 8 x 4 mm^3, 7.5 x 5 x 2 mm^3 and 19 x 9 x 3 mm^3, respectively.

The grown crystals were subjected to different characterization studies.

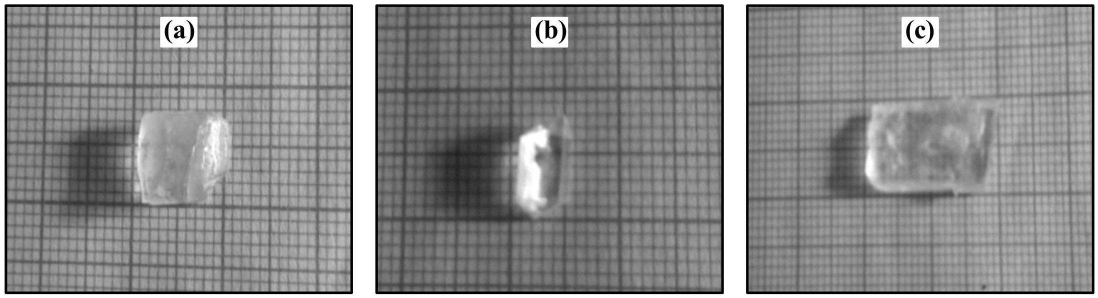

Fig. 1: (a) $ZnSO_4.H_2O$, (b) Glycine, (c) ZSG

RESULTS AND DISCUSSION

Results of various studies carried out with the grown crystals are discussed hereunder.

Powder X-ray diffraction

The powder XRD studies of grown crystals had been carried out using Richseifert diffractometer with CuKα (λ = 1.5406 Å) radiation. The recorded powder X-ray spectra of $ZnSO_4.H_2O$, glycine and ZSG are shown in Fig. 2.

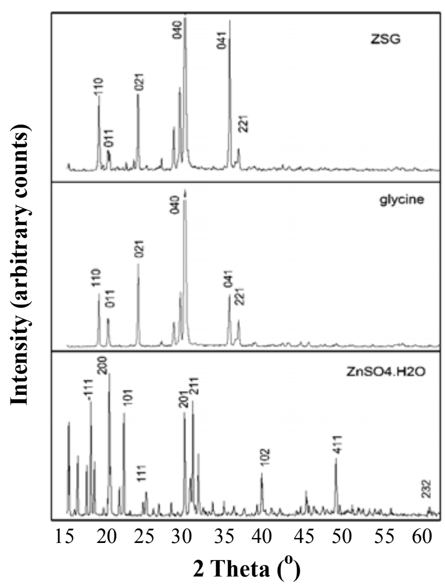

Fig. 2: Powder X-ray diffraction patterns of the grown crystals

All the reflections of powder XRD spectra are indexed with their corresponding hkl values using XPowder software[8-10]. The sharp peaks confirm the crystalline nature of the grown compounds.

Single XRD analysis

The grown crystals were subjected to single crystal XRD studies using a Bruker AXS diffractometer with MoKα radiation (λ = 0.71073 Å). The single crystal XRD reveals that all the three crystals belong to monoclinic system. The lattice parameter values are presented in Table 1 enabling a comparison. The results of this work are in good agreement with the reported values[3,7,10-12].

Table 1: Cell parameters of the grown crystals

Crystal	a(A^o)	b(A^o)	c(A^o)	α= γ	β	Cell volume (A^{o3})	Crystal system
Glycine	5.102	11.970	5.457	90^o	111^{o}42’	309.65	Monoclinic
$ZnSO_4.H_2O$	7.566	7.586	6.954	90^o	115^{o}56’	358.95	Monoclinic
ZSG	5.103	11.973	5.438	90^o	111.83^o	308.40	Monoclinic

UV-Visible spectral analysis

The optical transmission spectra of the grown crystals were recorded using Shimadzu UV-Vis spectrophotometer between the wavelength ranges of 200 and 800 nm and is shown in Fig. 3.

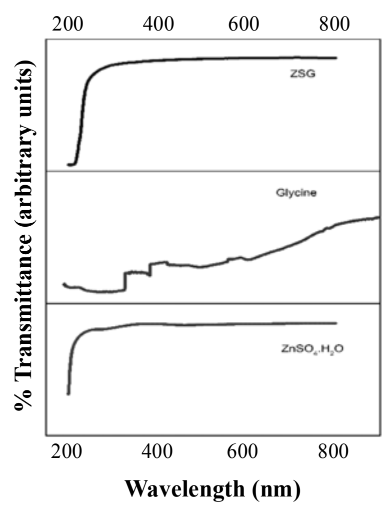

Fig. 3: UV-Visible spectrum of grown crystals

From the spectra, it is found that the grown ZSG is highly transparent in the wavelength range of 240-800 nm. The UV transparency cut-off wavelength is 236 nm as in[12]. The transparency of the grown ZSG was 85.39%, which showed a marked improvement in the transparency of glycine due to the role of dopant[3,10,11,13].

FTIR Spectral analysis

The FTIR spectra of the grown crystals of $ZnSO_4.H_2O$, glycine and ZSG had been recorded in the KBr phase in the frequency region 4000-400 cm^{-1} using Perkin Elmer spectrometer and are shown in Fig. 4 (a, b, and c), respectively.

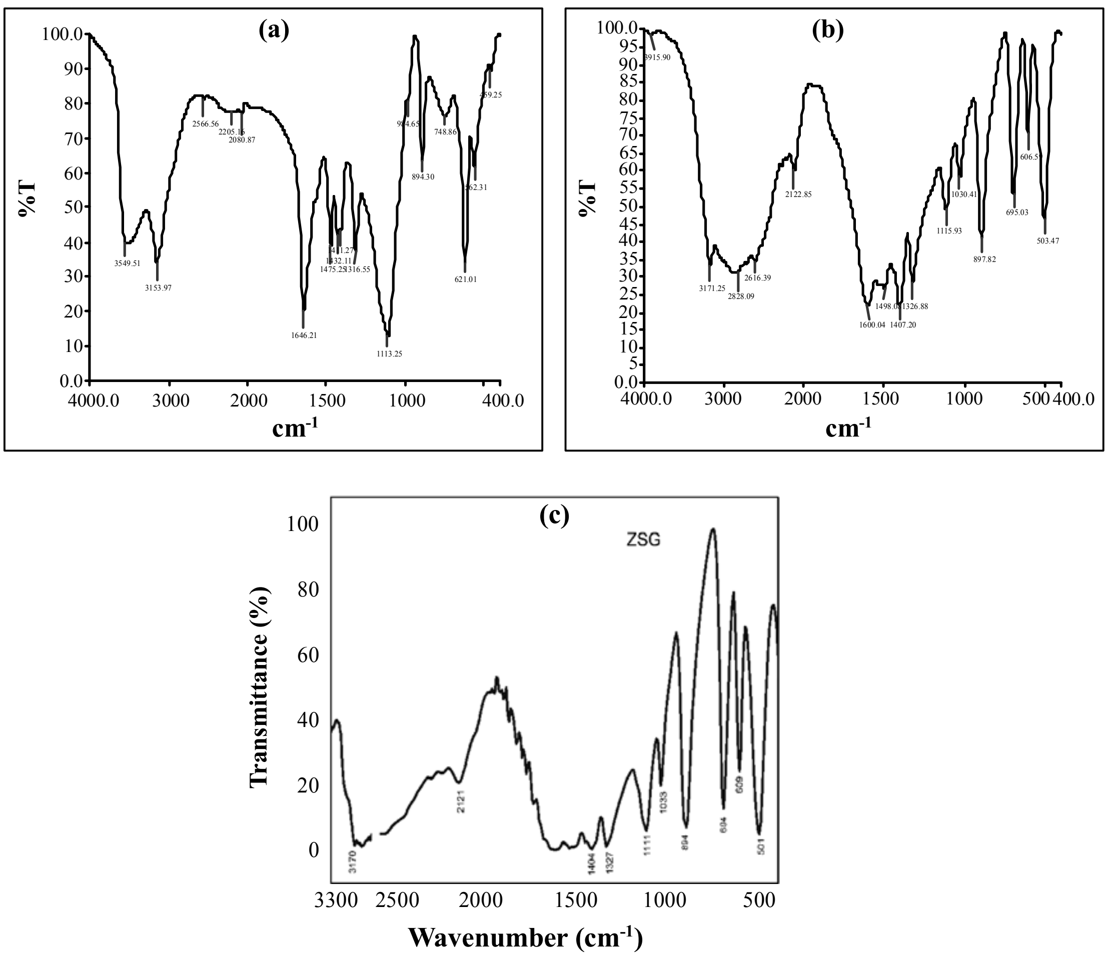

Fig. 4: (a) FTIR spectrum of $ZnSO_4.H_2O$, (b) FTIR spectrum of glycine, (c) FTIR spectrum of ZSG

Comparative vibrational frequency values of grown crystals are given in Table 2. The presence of NH_3^+ group is confirmed through the hydrogen bonded symmetric and asymmetric stretching vibrations. The absorption due to carboxylate group of glycine is observed at 503, 606, 695 and 1407 cm^{-1}.[14-16] In the ZSG these peaks are shifted to 501, 609, 694 and 1404 cm^{-1}, respectively. The peak at 3170 cm^{-1} is due to asymmetric stretching of CH_2.[17] Also the peak at 2121 cm^{-1} represents N-H stretching. The remaining peaks observed at 894 and 1033 cm^{-1} are due to C-C-N group[3,18,19]. Thus carboxyl group is present as carboxylate ion and amino group is present as ammonium ion in the grown ZSG. This observation confirms the existence of zwitter ionic form and the involvement of NH_3^+ in hydrogen bonding in the grown ZSG single crystal.

Table 2: FTIR spectral data of grown crystals

Mode of vibrations	Band assignments		
	$ZnSO_4.H_2O$	**glycine**	**ZSG**
O-H symmetric stretching mode	3549, 2566	2616, 2828	-
Bending of H-O-H	1642	-	-
Bending vibration mode of H_2O	748	-	-
Stretching of CH_2	-	2828, 3171	3170
N-H stretching	-	2122	2121
O-H bending	-	1407	-
S=O stretching	1316	-	-
S-O stretching	748	-	-
Sulphate ion	1113, 984, 621	-	-
Carboxylate group	-	1407, 695, 606, 503	1404, 694, 707, 609, 501
C-H	-	1327	1327
C-C-N	-	1030, 897	1033, 894
NH_3^+	-	-	3170, 1111

Thermal studies

Thermo gravimetric analysis (TGA) gave information regarding the distinctive aspects of thermal stability, phase transition, water of crystallization and thermal decomposition of the crystal. In general, TGA gives the upper temperature limit of a material within which it can be used[17,19]. TGA was carried out between 25ºC and 700ºC at a heating rate of 20ºC/min using Perkin-Elmer thermal analyzer STA409PC in nitrogen atmosphere. The resulting thermogram of ZSG is shown in Fig. 5.

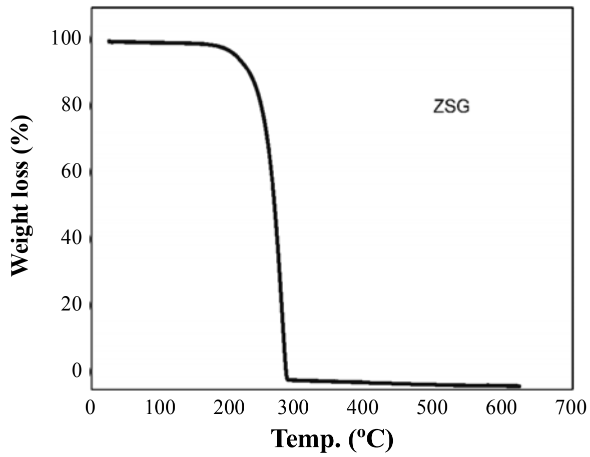

Fig. 5: TGA spectrum of ZSG

From TGA it is evident that the compound has good thermal stability up to 170°C as there is no detectable weight loss. Hence, it is evident that ZSG crystal had not included any solvent molecule during crystallization. This ensured that ZSG is suited for Laser applications[3,9]. From the graph, the melting point of ZSG was found to be 200°C, which was indicative of the good thermal stability. Since ZSG crystal can retain texture up to 200°C, it is more suitable than the other semi-organic materials like L-alanine cadmium chloride (110°C), triallyl thiourea cadmium chloride (101°C), triallyl thiourea cadmium bromide (97°C), triallyl thiourea mercury chloride (133°C) and allyl thiourea mercury bromide (125°C)[10, 11].

Vicker's micro hardness studies

The hardness of the crystals depends on type of chemical bonding, inter-atomic spacing, Debye temperature, lattice energy, and heat of formation. Most of these hardness predictors differ along the crystallographic directions. Vickers hardness test is the most common and reliable method for hardness measurement of solid surfaces[1].

The micro hardness of the grown crystals was measured using a Shimadzu Micro hardness Tester with a diamond indenter. In the present work, a well polished crystal was mounted on the platform of the micro-hardness tester and indentations were made on the grown crystals for three loads of 25 g, 50 g and 100 g with an indentation time of 10 seconds.

The length of the two diagonals of the mark made by the diamond indenter was measured. For a particular load, two well defined indentations were made and the average value (d) for each load was calculated.

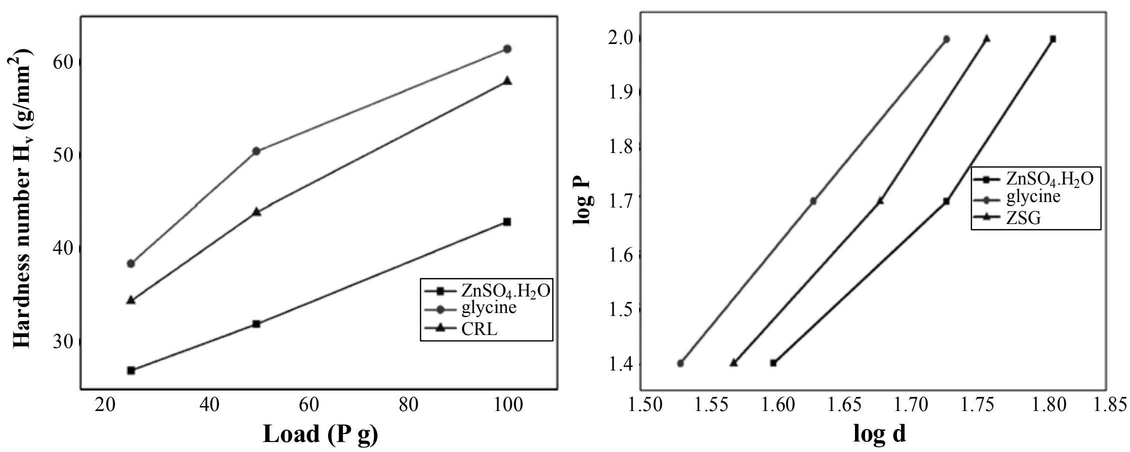

Fig. 6: (a) Plot between load P and H_V, (b) Plot between log d and log P

Vicker's hardness number was determined using the expression

$$H_v = 1.8544\ \frac{P}{d^2}$$

where, 'P' is the applied load, 'd' is the average diagonal length of the indentation marks. From the graph (Fig. 6a), it is clear that the hardness value increased with an increase in load. This behaviour proves that the grown crystal exhibits the Reverse Indentation Size Effect (RISE). According to the Meyer's law, the relation between the load and size of indentation is given by $P = k_1d^n$, where 'k_1' is the material constant, 'n' is the Meyer's index or work hardening coefficient[19,20].

The plot of log P against log d is shown in Fig. 6b, which gives a straight line (after least square fitting), from which the value of 'n' for $ZnSO_4.H_2O$, glycine and ZSG was found to be 2.3, 2.8 and 2.7, respectively. According to Onitsch and Hanneman, 'n' should lie between 1 and 1.6 for hard materials and should be above 1.6 for soft materials. Hence, all the three grown crystals belong to soft material category. This is in line with reported results for the parent materials ($ZnSO_4.H_2O$ and glycine). The value of Meyer's index 'n' of ZSG is 2.7; whereas n value of glycine is 2.8. The dopant $ZnSO_4.H_2O$ had reduced the value of n from 2.8 to 2.7. This reduction appears to be due to the absence of liquid inclusions and higher stress required to form dislocations[9, 10, 21].

CONCLUSION

Optically transparent, good quality single crystals of $ZnSO_4.H_2O$, glycine and ZSG were successfully grown by slow evaporation technique at room temperature. It was found that the dimension of the ZSG increased by doping. Powder XRD analysis revealed the crystalline nature of the grown crystals. Single crystal XRD revealed that the ZSG had acquired the structure of α glycine and it existed in zwitter ionic form, which resulted in the modifications of the properties. From the UV-Visible transmission spectrum, it was evident that the percentage of transmission (85.39%) was enhanced due to doping. This property can be used for optical applications. FTIR analysis identified the functional groups present in the grown single crystals. From the thermal studies, it was found that the doped crystal was stable up to 200°C and hence it may be useful for laser applications. The Vicker's micro hardness test showed that the hardness value of ZSG increased with the load, which confirmed the reverse indentation size effect and soft nature of the crystal. Results of these studies clearly confirm the improvement in optical, thermal and mechanical properties of ZSG crystals comparing with that of pure glycine and $ZnSO_4.H_2O$ crystals. Also due to these improved properties, this crystal finds its potential applications in the area of opto electronics.

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