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Spectral, thermal and hardness studies on unidirectional grown dichlorido diglycine zinc dihydrate single crystal

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ABSTRACT

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1. Introduction

The organic amino acid materials constitute a family in which glycine (CH₂COO⁻NH₃⁺) is the simplest of all the amino acids. It is the only amino acid without a center of chirality and has a high melting point due to its dipolar nature [1]. The glycine molecule is amphoteric in nature; however, it acts as unidentate ligand through the carboxylate group and it seems that the amino moiety is not involved in the metal coordination [2]. Recent literature reports show that glycine combines with metal salts like CaCl₂ [3], BaCl₂[4], SrCl₂[5], CoBr₂[6], ZnSO₄[7] and LiSO₄[8] and forms new complex materials. Zinc chloride dihydrate co-ordinates with glycine to form a complex material, dichlorido diglycine zinc dihydrate (DCDGZ), which crystallizes in the monoclinic crystal system with space group C2/c and lattice parameters a = 14.4167 Å, b = 6.9068 Å, c = 12.9531 Å and $\beta = 117.940^{\circ}$ [9]. The crystalline perfection has been studied using high resolution X-ray analysis that shows that the specimen has a low angular grain boundary spread around 14 arcsec [10]. Unidirectional crystal growth method has been established by Sankaranarayanan and Ramasamy [11] for the growth of single crystal with desired orientation at low temperature. This technique offers the main benefit of growing a crystal along a specific orientation instead of natural facets. It results in reducing the wasteful portion of the crystal for device applications and the high percentage of solute-solvent conversion efficiency [12,13]. Phase matching direction KDP crystal has been grown using this technique and has achieved 90% of usable yield for

Bulk semi-organic single crystal of dichlorido diglycine zinc dihydrate has been grown by unidirectional crystal growth method from aqueous solution. The phase of the grown crystal was identified using single crystal XRD analysis. The functional groups present in the crystal were confirmed using FTIR and ¹H NMR analysis. Transmission study shows 70% of transmission in the entire visible region, which reveals the good optical quality of the grown crystal. A stable broad peak in the range of violet–green emission was observed in the emission spectrum, which is due to the existence of defects in the crystal. The thermal and mechanical properties of the grown crystal were studied using TG/DTA and the Vickers microhardness tester, respectively.

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frequency conversion applications [14]. To the best of our knowledge, no reports are available on the growth of DCDGZ crystal using unidirectional solution growth method. In the present study, bulk single crystal of DCDGZ has been grown along $\langle 0 0 1 \rangle$ direction using unidirectional crystal growth method for the first time and has achieved enhanced crystal size of good optical quality. The phase of the grown crystal was confirmed by single crystal XRD analysis. The functional groups present in the crystal were confirmed by FTIR and ¹H NMR spectral analysis. The optical quality of the crystal was studied by transmission and emission spectra. In addition, a detailed discussion of thermal analysis and microhardness study are presented in this paper.

2. Experiment

2.1. Synthesis and solubility studies

The DCDGZ salt was synthesized according to the following reaction by mixing commercially available glycine and zinc chloride dihydrate (99.9%) in 2:1 molar ratio using double distilled water as solvent.

$$2CH_2NH_2COOH + ZnCl_2 \cdot 2H_2O \rightarrow (CH_2NH_3^+COO^-)_2ZnCl_2 \cdot 2H_2O$$
(1)

The resultant product of DCDGZ was purified by successive recrystallization process using double distilled water and care was taken to avoid decomposition during heating by maintaining the solution at 60 °C.

Solubility studies were carried out using the synthesized salt of DCDGZ and double distilled water as solvent. The solution was kept



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Fig. 2. Photograph of as-grown DCDGZ single crystal.

in a constant temperature bath maintained at 30 °C (accuracy \pm 0.05 °C) and continuously stirred using motorized magnetic stirrer, to have uniform temperature and concentration throughout the volume of the solution. After attaining supersaturation, the equilibrium concentration of the solute was analyzed gravimetrically [15]. The same procedure was repeated for various temperature ranges from 35 to 50 °C with 5 °C interval. The variation of solubility with temperature is shown in Fig. 1.

2.2. Crystal growth

Bulk growth has been adopted using unidirectional crystal growth method as reported by Sankaranarayan and Ramasamy [11] and the detailed description of the crystal growth setup is reported elsewhere [16]. According to the solubility data, the saturated solution was prepared at 38 °C. The prepared solution was filtered using Whatman filter paper of porosity 2.5 µm to remove extraneous solid colloidal particles that can act as a source of spontaneous nucleation. The filtered solution was overheated to 45 °C for 10 h, which further helps in reducing the possibility of nucleation during growth. Spontaneously obtained good quality seed of $\langle 0 0 1 \rangle$ direction was fitted at the bottom of the ampoule. The seed-fitted ampoule was immersed in the crystal growth setup at room temperature. To avoid thermal stress on the seed crystal the temperature of the bath was gradually raised up to the operating temperature. Upon reaching it, the saturated solution was filled in the ampoule. The temperature at the top and bottom of the ampoule was maintained at 42 and 38 °C, respectively, for the complete duration of the growth run, which helps to create a thermal gradient inside the growth apparatus. The concentration gradient gets shifted towards the seed crystal due to the action of gravity, which helps in the growth, and the concentration of the solution at the top keeps on increasing due to slow evaporation, which induces buoyancy convection that further helps in increasing the concentration towards the growing crystal. A crystal of size 108 mm length and 12 mm diameter was grown with an average growth rate of 3.6 mm per day. The photograph of as grown crystal is shown in Fig. 2.

3. Results and discussion

3.1. Single crystal X-ray analysis

The grown crystal was subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 single crystal X-ray diffractometer. The result shows that the crystal belongs to the monoclinic system with cell parameters a=14.414(2) Å, b=6.907(2) Å, c=12.953(2) Å, $\beta=117.99^{\circ}$ and point group 2/m and space group C2/c, which are in good agreement with the literature report [9].

3.2. FTIR analysis

The FTIR spectral analysis of the grown crystal was recorded in the range 400–4000 cm⁻¹ using Bruker IFS 66v spectrophotometer employing KBr pellet technique and the resultant spectrum is depicted in Fig. 3. The sharp peak at 3458 cm⁻¹ is due to the hydrogen bonded OH group. In comparison with the absorption due to the carboxylate group of γ -glycine observed at 608, 1397, and 1593 cm⁻¹, these peaks are found to be shifted at 602, 1395 and 1633 cm⁻¹, respectively, in the case of DCDGZ. Similarly, the peaks due the NH₃⁺ group of γ -glycine observed at 1133 and 3175 cm⁻¹ were shifted to 1137 and 3194 cm⁻¹, respectively, for DCDGZ. This observation confirms that glycine exists in the zwitterionic form. The comparison of IR bands with γ -glycine is shown in Table 1. The peaks at 1043, 903 and



Fig. 3. FTIR spectrum of DCDGZ single crystal.

Table 1	
FTIR spectral data for DCDGZ crystal.	

IR band (cm^{-1})		Assignment
γ-glycine	DCDGZ	
506 608 685 893 1044 1133 1336 1397 1593	502 602 706 903 1043 1137 1341 1395 1633	$ au(COO^{-})$ $\omega(COO^{-})$ $\delta(COO^{-})$ v(CC) $v_{a}(CCN)$ $v_{s}(NH_{3}^{*})$ $\omega(CH_{2})$ $v_{s}(COO^{-})$ $v_{2}(COO^{-})$
1438 2664 3000 3175 -	1444 2643 3014 3194 3458	$\delta(CH_2)$ $v_s(CH_2)$ $v_a(CH_2)$ $v_a(NH_3^*)$ $OH(H_2O)$

2643 $\rm cm^{-1}$ are attributed to CCN, CC and $\rm CH_2$ stretching groups of DCDGZ, respectively.

3.3. ¹H NMR spectral analysis

The ¹H NMR spectrum was recorded using Bruker Advance III 500 MHz FTNMR spectrophotometer using D₂O as solvent. The ¹H NMR spectrum of DCDGZ (Fig. 4) shows three characteristic peaks at 4.702 δ , 3.492 δ and 2.650 δ . The peaks at 4.702 δ and 3.492 δ are due to the hydrogen of NH₃⁺ and CH₂ (methylene) groups, respectively. The larger peak area of the amino group is due to the presence of three hydrogen atoms and the smaller peak area corresponds to methylene group that contains two hydrogen atoms. The water molecule peak is shifted downfield to 2.650 δ due to hydrogen bonding.

3.4. Transmission analysis

Optical properties of materials are important as they provide information on the electronic band structures, localized states and types of optical transitions. The cut and polished plate of the grown crystal was subjected to transmission measurements in the spectral region of 200–1100 nm using Varian Cary 5E spectrophotometer. Fig. 5 shows the transmission spectrum of DCDGZ crystal. The characteristic absorption peak is prominent at 250 nm, and there is no absorption between 250 and 1100 nm. The good transmission (80%) of the crystal in the entire visible region shows good optical quality of the grown crystal.

3.5. Photoluminescence studies

The photoluminescence spectrum was recorded using JOBIN YVON FLUROLOG-3-11 Spectroflurometer at room temperature.



Fig. 5. Transmission spectrum of DCDGZ.

The recorded emission spectrum of excitation wavelength 230 nm is shown in Fig. 6. A stable broad peak in the range of violet–green emission is observed in the room temperature photoluminescence. The broad peak ranges from 350 to 6000 nm with a maximum at 398 nm and the results indicate that DCDGZ crystal has violet emission. The maximum intensity that appears at 398 nm is attributed to $n-\pi^*$ transition of carbonyl group [17]. The peak found at 556 nm indicates green emission and may be assigned as $\pi-\pi^*$ transition due to the interaction between the metal (Zn²⁺) and ligand molecules [18]. The remaining small peaks at 439 nm may be attributed to the presence of unknown defects [19].

3.6. Thermal analysis

TG/DTA of the grown crystal was carried out between room temperature and 1000 °C at a heating rate of 10 °C/min using NETZSCH STA 409 C/CD in nitrogen atmosphere. The compound undergoes four stages of weight loss as observed in the TG curve at 130, 254, 586 and 720 °C as shown in Fig. 7. The following decomposition pattern has been formulated to account for the weight losses.

Step 1

 $(\text{NH}_3\text{CH}_2\text{COO})_2\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{91 \text{ to } 130^\circ\text{C}} (\text{NH}_3\text{CH}_2\text{COO})_2\text{ZnCl}_2 + 2\text{H}_2\text{O} \uparrow$ Formula weight = 322.48 36.0

Weight loss =
$$11.1\%$$



Step 2

$$(NH_3CH_2COO)_2ZnCl_2 \xrightarrow{130 \text{ to } 380 \circ C} ZnCO_3 + NH_4CNO + 2CH_3Cl \uparrow 2 \times 50.4$$

Weight loss = 31.3%

Step 3

 $ZnCO_{3} + NH_{4}CNO \xrightarrow{380 \text{ to } 700 \,^{\circ}C} Zn + HCN + CO_{2} \uparrow + NH_{3} \uparrow + O_{2} \uparrow$ Total mass unit = 92.0 Weight loss = 28.9%

Step 4

$$Zn + HCN \xrightarrow{> 700^{\circ}C} Zn + H\uparrow + CN\uparrow$$

Total mass unit = 27.0
Weight loss = 8.4%

The first experimental weight loss observed between 91 and 130 °C in the TG curve, corresponds to a weight loss of 11%, which is due to the evolution of two water molecules from the crystal system. The theoretical weight loss predicted from the formulated pattern is 11.17%. The second stage of weight loss of 31% observed at 254 °C is due to the elimination of two molecules of methyl chloride and formation of zinc carbonate and ammonium cyanate. The corresponding calculated theoretical weight loss is 31.3%. The third weight loss observed at 586 °C is due to the decomposition of ammonia, carbon dioxide, oxygen and formation of zinc and hydrogen cyanide. The experimental weight loss in this stage is 30%, which is almost equal to the theoretical weight loss of 28.9%. Finally, the weight loss of 8% at 720 °C is due to the decomposition of carbon and cyanide, the corresponding theoretical weight loss is 8.4%. The remaining 20% of residue is zinc. In all the four steps of decomposition, the differences between the experimental and the formulated weight losses Oare very small and in addition, it is evident from the TG study that the compound is formed in the stoichiometric ratio and the compound contains adsorbed water molecules. The differential thermal analysis curve depicts three exothermic peaks at 94, 134 and 231 °C. The first peak represents the evolution of one water molecule and the second peak is due to the elimination of the second water molecule and the third one is due to the evolution of methyl chloride. Furthermore, this analysis confirms that the crystal is thermally stable up to 91 °C.

3.7. Microhardness measurements

Hardness of the crystal carries information about the strength, molecular binding, yield strength and elastic constants of the material. The microhardness of DCDGZ crystal was determined using the Vickers microhardness tester fitted with a diamond pyramidal indenter. Indentations were made for the applied loads varying from 25 to 300 g for a constant time of 5 s and the diagonal lengths of the indented impressions were measured. The average diagonal length of the indented impressions was calculated and the Vickers microhardness number was found from the following relation:

$$Hv = 1854.4 \frac{P}{d^2} \, \text{kg/mm}^2 \tag{2}$$

where *P* is the applied load (in kg) and *d* is the average diagonal length of the indented impressions (in µm). The microhardness profile as a function of applied load is shown in Fig. 8. From the profile it is observed that the hardness of the crystal increases with applied load up to 150 g and becomes load independent for $P \ge 150$ g. This is due to the reverse indentation size effect [20]. The relationship between load and size of indentation is given by Meyer's law, $P=Ad^n$, where *P* is load, *d* is diagonal length of the impression, *A* and *n* are constants for a particular material [21]. The slope of log *P* vs. log *d* plot gives the



Fig. 9. Plot of log P vs. log d.

Table 2

Hardness parameters of DCI

Meyer index number (<i>n</i>)		Hardness H _v (Kg/mm ²)	<i>W</i> (g)	A_1 $(g/\mu m^2)$	Corrected hardness H_0
Low loads	High loads				(Kg/mm)
2.835	1.502	67	-19.87	0.039	72.3

Meyer's index number (*n*) and when the exponent n < 2 there is normal ISE behavior, when n > 2 there is a reverse ISE behavior and when n=2 the hardness is independent of the applied load, which is given by Kick's law. Fig. 9 shows the plot of log *P* vs. log *d* for the grown crystal and is presented by two segments in the plot for $P \le 150$ g and P > 150 g. The estimated values of *n* are shown in Table 2.

According to Onistch, for hard materials n lies between 1 and 1.6 and soft material it is above 1.6 [22]. So the values of n in Table 2 imply that DCDGZ is a hard crystal.

According to Hays–Kendall's approach load dependent hardness may be expressed by [23]

$$P = W + A_1 d^n \tag{3}$$

where *W* is the minimum load initiate plastic deformation, A_1 is the load independent constant and the exponent n=2. The values of *W* and A_1 can be calculated by plotting the experimental *P* against d^2 plot. These two values have been estimated from the plot drawn between *P* and d^2 as shown in Fig. 10. The corrected hardness H_0 has



been estimated using the relation:

 $H_0 = 1854.4A_1 \tag{4}$

The calculated hardness parameters are given in Table 2.

4. Conclusion

Optically good quality semi-organic single crystal dichlorido diglycine zinc dihydrate has been grown by unidirectional crystal growth method from aqueous solution. Single crystal X-ray analysis shows that the crystal belongs to the monoclinic system with lattice parameters a=14.414 Å, b=6.907 Å, c=12.953 Å and $\beta=117.99^{\circ}$. The presence of the functional groups was confirmed using FTIR and ¹H NMR analysis. Transmission study shows 70% of transmission in the entire visible region, which exhibits good optical quality of the grown crystal. A stable broad peak in the range of violet–green emission was observed in the emission spectrum, which is due to the existence of defects in the crystal. The thermal analysis shows that the crystal is thermally stable up to 91 °C. The microhardness measurement shows that the Vickers microhardness value is 72 kg/mm².

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References

- K. Ambujam, S. Selvakumar, D. Prem Anand, G. Mohammad, P. Sagayaraj, Cryst. Res. Technol. 41 (2006) 671.
- [2] A. Bismondo, L. Rizzo, G. Tomat, D. Curto, P. Di Bernardo, A. Cassol, Inorg. Chim. Acta 74 (1983) 21.
- [3] J.K. Mohan Rao, M.A. Vishwamithra, Acta Crystallogr. Sect. B 28 (1972) 1484.
- S. Natarajan, J.K.Mohan Rao, Z. Kristallogr. 152 (1980) 179.
 S. Natarajan, K. Ravikumar, S.S. Rajan, Z. Kristallogr. 168 (1984) 75.
- [6] K. Ravikumar, S.S. Rajan, S. Natarajan, M.N. Ponnuswamy, J.Z. Trotter, Z. Kristallogr. 171 (1985) 201.
- [7] M. Fleck, L. Bohaty, Acta Crystallogr. C60 (2004) m291.
- [8] M.R. Suresh Kumar, H.J. Ravindra, S.M. Dharmaprakash, J. Cryst. Growth 306 (2007) 361.
- [9] S.Mary Navis Priya, B. Varghese, J. Mary Linet, S. Jerome Das, Acta Crystallogr. E63 (2007) m2318.
- [10] S.Mary Navis Priya, B. Varghese, J. Mary Linet, G. Bhagavannarayana, C. Justin Raj, S. Krishnan, S. Dinakaran, S. Jerome Das, Cryst. Growth Des. 8 (2008) 1663.
- [11] K. Sankaranarayanan, P. Ramasamy, J. Cryst. Growth 280 (2005) 467.
- [12] K. Sankaranarayanan, J. Cryst. Growth 284 (2005) 203.
- [13] R. Ramash Babu, K. Sethuraman, R. Gopalakrishnan, P. Ramasamy, J. Cryst. Growth 297 (2006) 356.
- [14] P.M. Ushasree, R. Muralidharan, R. Jeyavel, P. Ramasamy, J. Cryst. Growth 210 (2000) 741.
- S. Dinakaran, Sunil Verma, S. Jerome Das, S. Kar, K.S. Bartwal, P.K. Gupta, Phys. B: Condens. Matter 405 (2010) 1809.
- [16] J. Mary Linet, S. Jerome Das, Phys. B: Condens. Matter 405 (2010) 3955.
- [17] C. Laurent, F. Massines, C. Mayoux, D.M. Ryder, C. Olliff, IEEE Conf. (1995) 93.
- [18] P. Mythili, T. Kanagasekaran, S. Stella Mary, D. Kanjilal, R. Gopalakrishnan, Nucl. Instrum. Methods Phys. Res. B 266 (2008) 1737.
- [19] A. Meijerink, G. Blasse, M. Glasbeek, J. Phys. Condens. Matter 2 (1990) 6303.
- [20] P. Mythili, T. Kanagasekaran, N. Shailesh, R. Sharma, Gopalakrishnan, J. Cryst. Growth 306 (2007) 344.
- [21] A. Abu El-Fadl, A.S. Soltan, N.M. Shaalan, Cryst. Res. Technol. 42 (2007) 364.
- [22] S. Mukerji, T. Kar, Cryst. Res. Technol. 34 (1999) 1323.
- [23] K. Sangwal, A. Klos, Cryst. Res.Technol. 40 (2005) 429.