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Effect of ZnO and co-doped ZnO additive in the growth, structural, optical and mechanical properties of glycine single crystals

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Abstract - *The interest towards the amino organic zinc oxide compounds with water as solvent persuaded to do this investigation. The growth and characterization of single crystals of simplest amino acid, glycine from aqueous solution in the presence of zinc oxide and co-doped zinc oxide (co-dopant: Na and K) as an additive using slow evaporation technique were carried out. The influence of additives in the growth atmosphere enhanced the crystal quality as well as their properties. Single crystal X-ray diffraction analysis was carried out to determine the lattice parameters of glycine with ZnO as an additive. EDAX analysis and Powder X-ray diffraction confirmed the presence of additives, which preserve the basic crystal structure of the parent compound. The various fundamental functional groups present in the title crystal were identified using FTIR spectral assignments. From UV-Vis analysis, increased absorption in the UV region and optical transmission in the entire visible region were observed. The mechanical strength of the grown crystals was estimated from Vickers micro hardness testing.*

Keywords *- Slow evaporation; Glycine; co-dopant; Single crystal; FTIR; EDAX*

I. INTRODUCTION

With modern technology, crystalline semi-organic materials play an important role in the fabrication of active and passive photonic devices. The amino acid group materials have been mixed with inorganic salts to form adducts or complexes in order to improve their mechanical and optical properties. The crystallization behaviour of the simplest amino organic glycine has been the subject of interest due to its importance in practical applications, especially in terms of understanding their role with respect to inorganic and organic materials. In past years, many glycine derivatives were extensively studied for its NLO properties, electroluminescence, photovoltaic, molecular electronics and optoelectronic technologies. Some complexes of glycine with inorganic salts like zinc chloride [1,2], zinc sulphate, lithium sulphate, nickel dichloride [3,4], zinc acetate [5], lithium chloride [6], calcium chloride [7], barium chloride, strontium chloride, magnesium chloride [8], cobalt bromide [9], potassium sulphate [10], silver nitrate [11], sodium nitrate [12,13,14] have been already reported. The complexes of glycine with inorganic salts, especially with ZnO are not explored very much for their physical and optical properties [15]. More recently, apart from the fundamental novelty of ZnO, there has been a discernible shift in interest towards the organo zinc oxide compounds with water as solvent which remains an area essentially little explored and undeveloped. The growth, physical and optical properties of glycine single crystals from aqueous solution in the presence of ZnO and co-doped ZnO as an additive in slow solvent evaporation technique were presented in this investigation.

II. EXPERIMENTAL PROCEDURE

A. Materials

The starting material glycine of 99.999% pure electrophoresis grade was obtained from Sigma Aldrich. Zinc oxide, sodium chloride and potassium chloride of AR grade and double distilled water were used for the crystal growth.

B. Crystal Growth

An optimized quantity of glycine was taken in a beaker. A proportionate amount of glycine and ZnO were mixed in another beaker. To prepare co-doped ZnO, the co-dopants NaCl and KCl were added in 2:1 ratio with ZnO. All the solutes were dissolved in double distilled water and continuously stirred for 1 hour to obtain homogenous solutions. The prepared mixtures were filtered, covered and kept in a dust free environment. In a span of 30 to 45 days, transparent and colourless single crystals were harvested. The photographs of the as grown crystals were shown in figure-1.

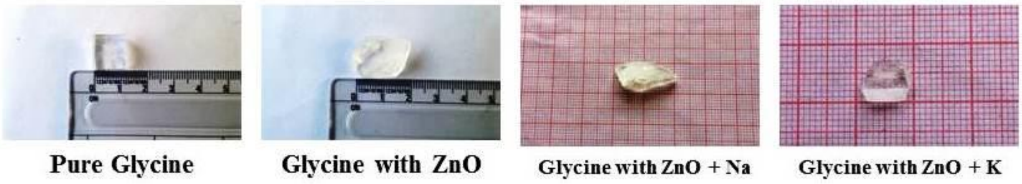

Pure Glycine
Glycine with ZnO
Glycine with ZnO + Na
Glycine with ZnO + K

Figure 1. As grown crystals

III. CHARACTERIZATION

A. Single-crystal X-ray diffraction

Single crystal x-ray diffraction was recorded using Bruker - AXS D8 - QUEST diffractometer to reveal the crystal structure and unit cell dimensions of the ZnO additive glycine crystal. From the crystal structure data, it was predicted that the as grown crystal belonged to α-glycine single crystal with monoclinic system having space group P21/n. The single crystal x-ray diffraction data and structure refinement were presented in table-1. Figure-2 shows the thermal ellipsoid plot using ORTEP3 drawn at 50% probability along with atom numbering scheme and figure-3 displays the packing of molecules in the unit cell viewed down along the a-axis using VESTA.

Table 1. Crystal data and structure refinement for ZnO additive glycine

Formula weight	75.07 g/mol
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 5.0977(16) Å α = 90° b = 11.953(4) Å β = 111.676(15)° c = 5.459(2) Å γ = 90°
Volume	309.1(2) Å^3
Z	4
Density (calculated)	1.613 Mg/m^3

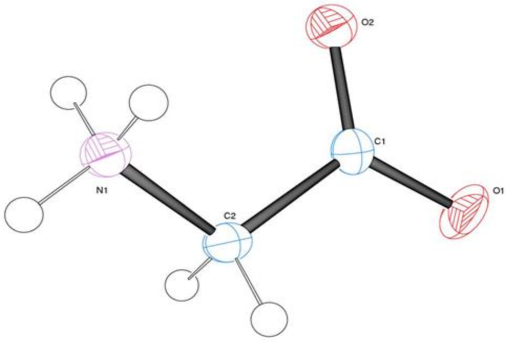


Fig 2. Thermal ellipsoid plot of ZnO additive glycine using ORTEP3

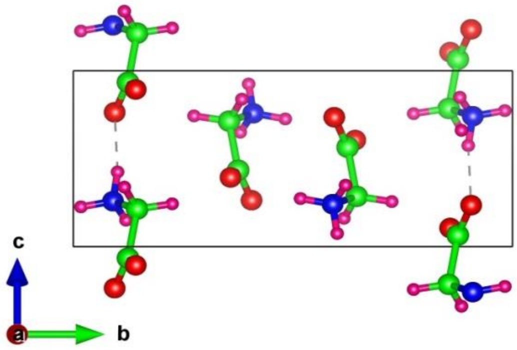
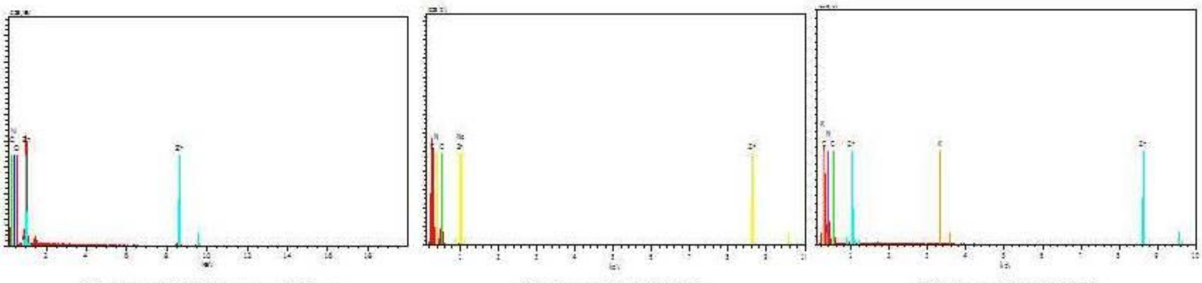


Fig 3. Packing of ZnO additive glycine molecules in the unit cell viewed down the a - axis using VESTA

B. EDAX analysis

Using a Quanta-FEG250 dispersive spectrometer, the EDAX spectra of zinc and co-doped zinc additive glycine crystals were studied. The percentage of elemental composition present in the as grown crystals was tabulated in table-2 and EDAX spectra of harvested doped and co-doped ZnO additive glycine crystals were shown in figure-4.



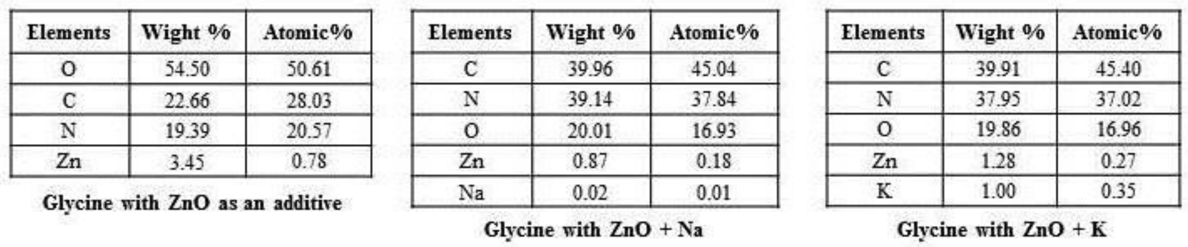
Glycine with ZnO as an additive

Glycine with ZnO + Na

Glycine with ZnO + K

Figure 4. EDAX spectra of as grown glycine crystals

Table 2. Elemental composition of as grown doped and co-doped ZnO additive glycine crystals from EDAX spectra



Elements	Wight %	Atomic%
O	54.50	50.61
C	22.66	28.03
N	19.39	20.57
Zn	3.45	0.78

Glycine with ZnO as an additive

Elements	Wight %	Atomic%
C	39.96	45.04
N	39.14	37.84
O	20.01	16.93
Zn	0.87	0.18
Na	0.02	0.01

Glycine with ZnO + Na

Elements	Wight %	Atomic%
C	39.91	45.40
N	37.95	37.02
O	19.86	16.96
Zn	1.28	0.27
K	1.00	0.35

Glycine with ZnO + K

C. Powder x-ray diffraction

Powder x-ray diffraction studies were carried out using Bruker D8 diffractometer with CuKα radiation (λ=1.54056 Å). The observed XRD patterns confirmed the good crystalline nature of the as grown crystals which were shown in figure-5. In the pure glycine crystal the ($\bar{1}$ 2 1) plane has maximum intensity and with additives, (0 4 0) plane has maximum intensity which was very well matched with JCPDS file no: 32-1702. A shift in the maximum intensity peak for pure glycine crystal was due to the change in growth plane which ascribed the morphological change in the harvested crystal. In all other reported works, due to the doping of molecules either the polymorphisms of the glycine crystals have been changed [16, 17, 18] or the dopant molecules entered into the crystal lattice and changed the crystal structure. [19, 20, 21]. In the present work, though the inclusion of ZnO altered the morphology, it preserved the basic crystal structure of glycine single crystal.

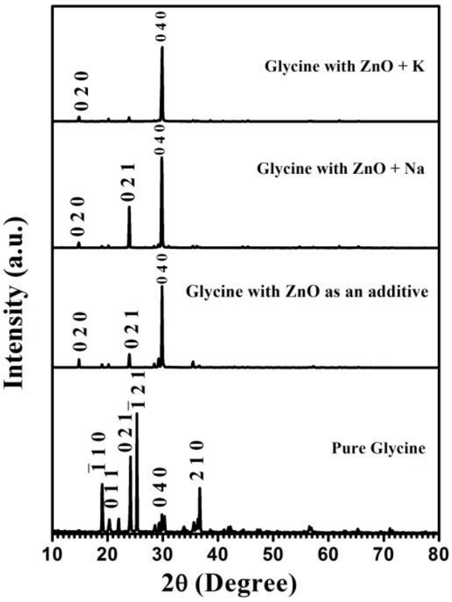


Figure 5. Powder XRD Patterns

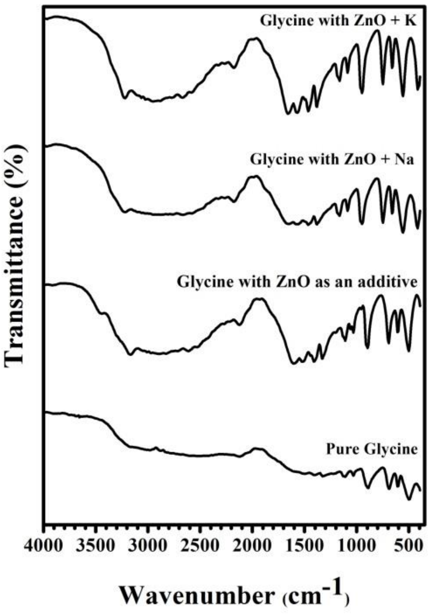


Figure 6. FTIR spectra

D. FTIR analysis

The FTIR spectra of pure glycine, doped and co-doped zinc additive glycine crystals were recorded using SHIMADZU FTIR spectrometer in the range of 400 – 4000 cm^{-1} by KBr pellet technique. It was shown in figure-6. The IR absorption spectrum of pure glycine was exactly coincided with earlier report [22]. The absorption peaks characterizing different functional groups were assigned in table-3 [23]. The peak at 424 cm^{-1} was observed for glycine with co-doped ZnO (co-dopant was sodium and potassium) which correspond to Zn-O stretching vibrations [24]. The inclusion of ZnO peak ensured the capping between ZnO and glycine molecules.

E. UV-Visible spectrum

For pure glycine, doped and co-doped zinc additive glycine, the UV-Visible spectral studies were carried out between 200 nm to 800 nm range and they were displayed in figure-7. The absorption was found in the UV region of 200 nm to 360 nm for pure glycine. But for doped and co-doped zinc additive glycine the absorption was found to be high and its range increased to 390 nm and possessed good transparency in the visible region.

Table 3. FTIR spectral assignments

Vibrational Modes	**Frequency in wavenumber (cm^{-1})**		
	Pure glycine	**ZnO additive glycine**	**Co-doped ZnO additive glycine**
NH$_2$ Asymmetric Stretching	-	344 (w)	-
NH$_2$ Symmetric Stretching	-	3170 (s)	3223 (s)
CH Symmetric Stretching	2978 (vw)	-	-
Combination band **(NH$_2$** Bending **+ CH$_2$** scissoring**)**	2122 (vw)	2122 (s)	2180 (s)
NH$_2$ Scissoring	-	1605 (s)	1657 (s)
OH Bending	-	1520 (s)	1562 (s)
CH$_2$ Scissoring	1404 (w)	1412 (s)	1468 (s)
CH$_2$ Twist	1327 (w)	1327 (s)	1372 (s)
CH$_2$ Rocking	1111 (w)	1111 (s)	1170 (s)
C-CN Asymmetric stretching	1034 (vw)	1034 (w)	1087 (s)
NH$_2$ Twisting	887 (s)	894 (vs)	949 (vs)
NH$_2$ Bending	694 (s)	694 (vs)	748 (vs)
COOH Bending	609 (s)	609 (s)	655 (vs)
CH$_2$ Bending	501 (s)	501 (vs)	555 (vs)
Zn-O Stretching	-	-	424 (vs)

w – weak, vw – very weak, s – strong, vs – very strong

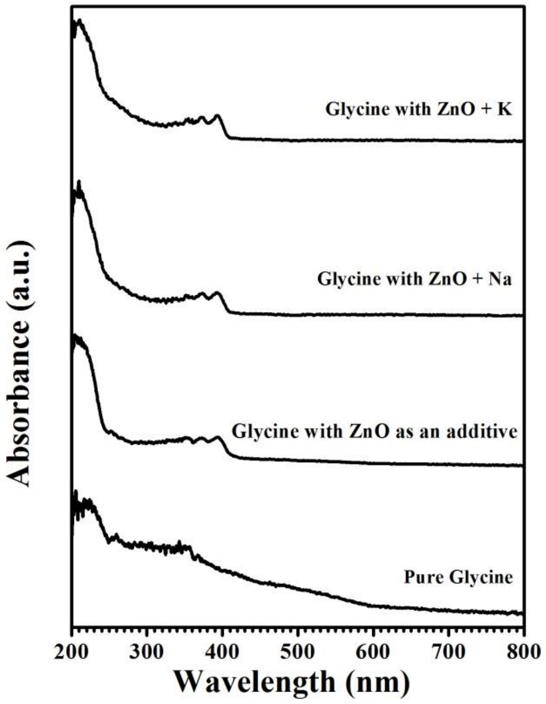


Figure 7. UV-Visible optical absorbance spectrum

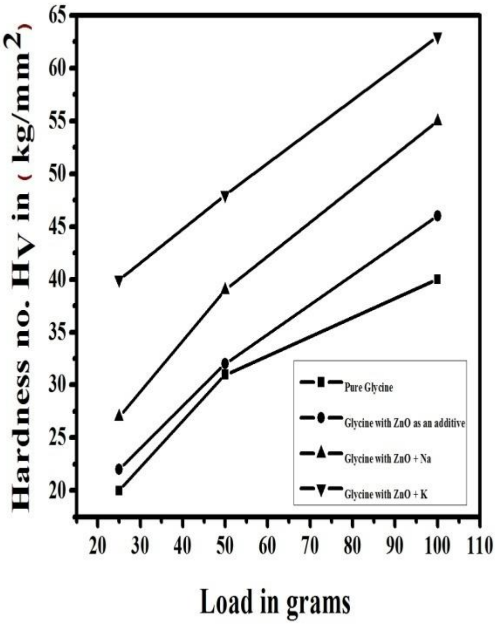


Figure 8. Load vs. Vickers hardness H_V

F. Microhardness studies

The Vicker's hardness number was calculated for all the as grown crystals using the relation $H_v = 1.8544 (P) / d^2$ (kg/mm^2) where H_v is the Vicker's hardness number, P is the applied load and d is the diagonal average length of the indentation impression. The plot between hardness number and the load was depicted in the figure-8. The value of microhardness number was increased with increasing load and at about 100 grams, cracks developed on the smooth surface of the crystal due to the release of internal stresses generated locally by indentation. The strength of the grown crystals was found to be increased with doped and co-doped ZnO addition.

IV. CONCLUSION

Pure, doped and co-doped zinc oxide additive glycine single crystals were grown by slow evaporation technique. From EDAX, powder XRD and single crystal x-ray diffraction studies, it was concluded that the doped and the co-doped zinc oxide additive did not alter the crystal structure of glycine but its presence changed the crystal morphology which was corroborated by the shift of maximum intensity peaks. In FTIR, the characteristic vibration peaks got shifted with increasing absorption impinging the influence of additive in the parent crystal and the ZnO peak ensured the capping of zinc oxide by glycine molecule which led to the tuning of properties of glycine single crystals. The high absorption in the UV region and good transparent window in the visible region of the doped and co-doped ZnO additive crystals more than the pure glycine crystal, made the material most suitable for photonics applications. The hardness of the doped and co-doped ZnO additive glycine crystal was found to be higher than the pure glycine crystal. The increase in the mechanical strength will have a significant effect on the fabrication of devices.

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