

## Article

# Croconic Acid Doped Glycine Single Crystals: Growth, Crystal Structure, UV-Vis, FTIR, Raman and Photoluminescence Spectroscopy

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**Abstract:** Glycine (Gly) single crystals doped with croconic acid (CA) were grown by evaporation from aqueous solutions. Depending on the weight ratio of Gly and CA in solutions, the crystals take on a plate or pyramidal shape. Both powder and single crystal XRD analyses indicate that the crystal lattices of plates ( $\alpha$ -Gly:CA) and pyramids ( $\gamma$ -Gly:CA) correspond to the lattices of pure  $\alpha$ -Gly and  $\gamma$ -Gly polymorphs, respectively. Raman and FTIR spectra of Gly:CA crystals are very close to the spectra of undoped crystals, but include bands associated with CA impurity. Analysis of UV-Vis absorption spectra indicates that doping does not remarkably change bandgap value  $E_g \sim 5.2$  eV but results in appearance of strong absorption bands in the transparency region of pure glycine crystals, which result from local electronic transitions. Incorporation of CA molecules in Gly creates strong green photoluminescence in a wide spectral range 1.6–3.6 eV. Comparison of the optical spectra of Gly:CA and previously studied TGS:CA crystals indicates that in both cases, the modifications of the optical spectra induced by CA doping are practically identical and are related to the interaction between CA molecules located in the pores of the host Gly crystals and neighboring Gly molecules.

**Keywords:** glycine; polymorphism; croconic acid; crystal structure; XRD; FTIR and Raman spectroscopy; UV-Vis absorption; photoluminescence



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## 1. Introduction

Protein amino acid glycine (Gly)  $\text{NH}_2\text{-CH}_2\text{-COOH}$  was discovered in 1820 by the chemist, botanist, and pharmacist Henri Braconnot. It was the first case wherein a pure amino acid was obtained from a protein [1]. Since glycine is produced in the human body during metabolism, it is safe and is widely used in medicine as a metabolic regulator that normalizes and activates protective inhibition processes in the central nervous system and reduces psycho-emotional stress.

Piezoelectricity is in increasing demand as it provides diverse entries into electronic, electromechanical, optical, and optoelectronic applications. A very high polarization response, which is promising for capacitors, memories, and piezoelectric applications, has been discovered mostly in inorganic oxides containing toxic lead or rare elements. Purely organic ferroelectrics, which are expected to be used as key materials in organic, printable, and bendable electronic device applications, are being pursued as possible alternatives. Recently, it was demonstrated that a basic component of biological structure,  $\gamma$ -glycine, presents nanoscale ferroelectricity, with an exhibited technologically significant piezoelectric response. Glycine is one of the simplest and smallest biological molecules.

It therefore presents a starting point for the design of functional materials as it can be synthetically modified to optimize properties.

Crystallization of glycine is characterized by polymorphism. Currently,  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -Gly modifications of glycine crystal structure are known. The most stable among them are  $\alpha$ - and  $\gamma$ -modifications. It is believed that the  $\alpha$  modification is the most stable one because  $\gamma$ - and  $\beta$ -glycine are transformed to  $\alpha$ -glycine at certain conditions. However, there exists an opposite perspective in the literature, which relates the  $\gamma$ -modification to the most stable one [2].  $\Gamma$ -Gly transforms in  $\alpha$ -Gly at  $T \approx 460$  K [3,4].  $\beta$ -Gly transforms in  $\alpha$ -Gly or  $\gamma$ -Gly at ambient conditions [2]. Similarly, under high pressure, phase transitions of  $\beta$ -Gly to  $\delta$ -Gly and  $\gamma$ -Gly to  $\epsilon$ -Gly occur [5].

$\alpha$ -Gly crystallizes in centrosymmetric crystal structure [space group  $P2_1/n$  (14)]. In contrast,  $\beta$ - and  $\gamma$ -Gly crystallize in non-centrosymmetric structure of monoclinic [sp.gr.  $P2_1$  (4)], and trigonal [sp.gr.  $P3_2$  (145) or  $P3_1$  (144)] symmetry, respectively [2–7]. Nominally pure glycine single crystals are transparent in a wide spectral range. Strong increase of absorption due to band-to-band electronic transitions begins in ultraviolet (UV) region for the light wavelength  $\lambda$  shorter than cut-off wavelength  $\lambda_{gap}$ . In both  $\alpha$ -Gly [8] and  $\gamma$ -Gly [9–12]  $\lambda_{gap} \approx 240$  nm. Estimations of the bandgap  $E_g$  are based on use of Tauc plot and provide the values of  $E_g = 5.11 \pm 0.02$  eV in  $\alpha$ -Gly [8] and  $E_g = 5.09$ – $5.3$  eV in  $\gamma$ -Gly [11–13]. A much higher value of  $E_g = 6.2$  eV has been reported in Ref. [14].

Non-centrosymmetric  $\gamma$ -Gly attracts much attention due to remarkable piezoelectric, pyroelectric, and non-linear optical (NLO) properties. The longitudinal piezoelectric coefficient  $d_{33}$  value for the  $\gamma$ -Gly crystals was discovered to be  $d_{33} = 7.37$  pC/N [13], piezoelectric strain constant  $\sim 9.93$  pm $\cdot$ V $^{-1}$  [15], pyroelectric coefficient  $p \sim 13$ – $21.4$   $\mu$ C/m $^2$ K [16,17]. The large value of piezoelectric coefficient makes  $\gamma$ -Gly an attractive material for design of flexible amino acid-based energy harvesting [18]. The glycine polycrystalline sensors indicate the effective piezoelectric constants of  $d_{33} = 0.9$  pC/N and of  $g_{33} = 60$  mV $\cdot$ m/N, respectively. Note that the latter one exceeds that of commercial piezoelectric lead zirconium titanate (PZT) [18].

Since glycine crystals grow from aqueous solutions, the addition of various substances to solutions makes it possible to significantly influence the process of glycine crystallization and obtain doped glycine crystals with modified physical properties. In particular, the type of additive and its amount can determine what polymorph of glycine will grow from solution. It was demonstrated in [19] that the addition to the solution of a small amount of zinc sulphate  $ZnSO_4$  with a molar concentration (0.2–0.4 M) is accompanied by growth of  $\alpha$ -Gly, and an increase in concentration (0.6–1 M) leads to the appearance of the  $\gamma$ -polymorph. In [20], the effects of seven common salts on primary nucleation of the metastable  $\alpha$ -Gly and the stable  $\gamma$ -Gly were studied. It was demonstrated that addition of  $(NH_4)_2SO_4$ , NaCl and  $KNO_3$ , in general, results in primary nucleation of  $\gamma$ -Gly simultaneously inhibiting  $\alpha$ -Gly primary nucleation. Addition of  $Ca(NO_3)_2$  and  $MgSO_4$  also promotes  $\gamma$ -Gly and inhibits  $\alpha$ -Gly primary nucleation but not sufficiently to induce  $\gamma$ -Gly.  $Na_2SO_4$  and  $K_2SO_4$  promote not only  $\gamma$ -Gly but also  $\alpha$ -Gly primary nucleation.

Polymorphic control of glycine by using the microdroplet technique for NaCl additive was investigated in [21]. Analysis of thermodynamics and nucleation kinetics of glycine polymorphs in microdroplets indicates that NaCl reduces the nucleation energy barrier of the  $\gamma$ -form of glycine, and for the same form of glycine, crystallization by the conventional method has a higher interfacial tension than in microdroplets.

Comparison of the crystallization process of glycine polymorphs and its salts/co-crystals in the presence of organic carboxylic acids through implementation of several different preparative techniques was studied in [6]. It was discovered that for the outcome of crystallization in “glycine– carboxylic acid” systems upon slow evaporation of aqueous solutions, both the choice of the acid and its concentration are of importance.

Additives can also influence a morphology of glycine crystals. As indicated in [22], the  $\gamma$ -Gly crystals grown from the solution containing glycine and sodium fluoride, sodium hydroxide, or sodium acetate had only three well developed faces (101), (0–11), and (–111)

with the remaining faces developed in the form of a pyramid. In contrast, adding to the solution of sodium nitrate resulted in a different morphology with four well-developed faces.

It is important that additions can strongly affect a nonlinear properties of glycine crystals. It was determined that the addition of alkali metal nitrides, bromides, chlorides, or acetates to a solution can significantly change the second-harmonic generation (SHG) efficiency in  $\gamma$ -Gly [11,23–25], reaching a maximum value for Cs chloride 5.06 times higher than that in a potassium dihydrogen phosphate (KDP) crystal [26].

From aqueous solutions of glycine with various inorganic and organic acids and salts, many new crystals were obtained [6,7], particularly the well-known ferroelectric triglycine sulfate (TGS), which has record values of the pyroelectric coefficient [27], and other ferroelectric crystals based on glycine and methylated glycine [7,28,29].

The effect of organic croconic acid (CA) additives on the glycine crystallization process has not yet been studied. Croconic acid crystals are a promising material in which CA molecules bonded by O-H...O hydrogen bonds provide excellent ferroelectricity at room temperature (RT) [30]. However, CA is corrosive and requires another acid in the solution to crystallize. In this regard, it is of considerable interest to study the properties of mixed Gly-CA crystals. The CA molecule,  $C_5H_2O_5$ , belongs to a series of planar monocyclic  $C_nH_2O_n$  oxocarbon acids. It has highly symmetric ( $D_{5h}$ ) plane topology and large value of molecular dipole momentum  $d \sim (9\text{--}10)$  D [30]. CA molecule is small and may be incorporated into the host lattice as an impurity in a wide concentration range.

It was recently discovered that doping above RT ferroelectric TGS crystals with CA molecules results in appearance of a strong green luminescence band in region of photon energy  $E_{ph} = 1.6\text{--}3.5$  eV with the band maximum at  $E_{ph} = 2.55$  eV. The doping also leads to the appearance of absorption bands related to local optical transitions in the transparency region of nominally pure TGS crystals and change of dielectric hysteresis loops [31]. CA doping does not change significantly TGS crystal structure, does not result in appearance of new phases, and does not influence frequencies of molecular vibrations measured by Raman and Fourier-transform infrared spectroscopy (FTIR).

Since, unlike TGS (which includes ordinary glycinium ions, zwitterions, and sulfuric acid molecules), glycine crystals are formed only by glycine zwitterions; the crystal structure of glycine can be either centrosymmetric ( $\alpha$ -Gly) or non-centrosymmetric ( $\gamma$ -Gly). It is interesting to compare the changes in the crystal structure, luminescence, and optical absorption caused by doping TGS and Gly crystals with croconic acid. For these reasons, in this work Gly single crystals were grown from aqueous solutions of glycine and croconic acid at the same relative ratios (80:20, 90:10, 98:2) as in previous studies of TGS:CA crystals.

Particularly, the primary questions of interest for the present study were the following: how does CA doping affect the crystal structure, crystal morphology, unit cell parameters of various glycine isomorphs, the amplitudes and frequencies of glycine molecular vibrations, the electronic band structure, in particular, the value of the band gap  $E_g$ , optical properties including absorption and luminescence spectroscopy of doped crystals. Generally, the aim of this research was the synthesis of CA-doped  $\alpha$ - and  $\gamma$ -Gly single crystals and the study of their structural and optical properties. Preliminary results on Raman and photoluminescence spectroscopy were presented in our conference paper [32].

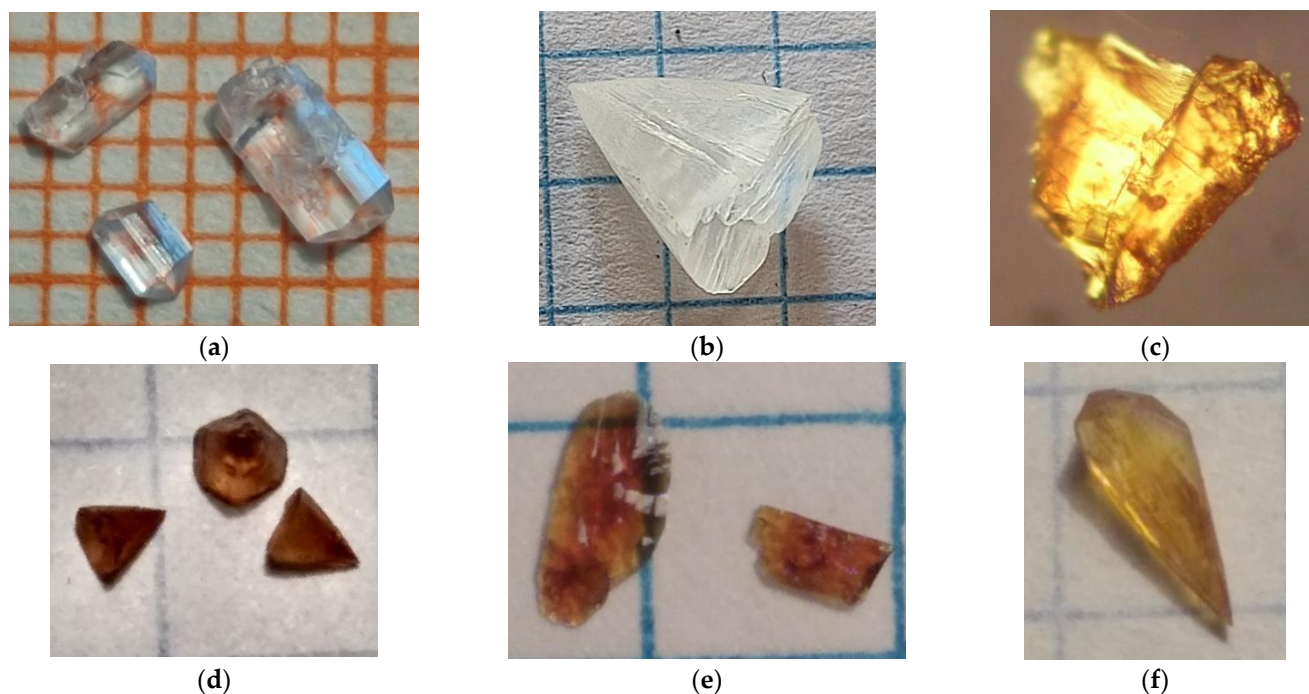
## 2. Materials and Methods

### 2.1. Crystal Synthesis

Figure 1 presents images of crystals used in this research. Nominally pure single crystals of  $\alpha$ -Gly were grown by evaporation from saturated aqueous solutions of aminoacetic acid ( $\alpha$ -Gly) (Figure 1a). Colorless “pure”  $\gamma$ -Gly crystals were grown from aqueous solution of  $\alpha$ -Gly crystals with adding 5% of citric acid  $C_6H_8O_7$  and may contain a small admixture of the acid (Figure 1b). Croconic acid crystals (Figure 1c) were prepared from the CA reagent (Alfa Aesar B21809, 98% purity) according to the procedure described in [33].

Croconic acid doped Gly crystals were grown from aqueous solutions with different weight ratios of Gly and CA—80:20, 90:10, 98:2. Gly:CA crystals grown from 80:20 and

98:2 solutions have a pyramidal shape with a hexagonal base (Figure 1d,f) analogous to nominally pure  $\gamma$ -Gly (Figure 1b). Crystals grown from 90:10 solution have plate shape like pure  $\alpha$ -Gly (Figure 1a).



**Figure 1.** Images of crystals used in this research.  $\alpha$ -Gly crystals grown from aqueous solution (a).  $\gamma$ -Gly crystal grown from aqueous solution with adding 5% of citric acid C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> (b). Croconic acid crystal (c). Gly:CA crystals grown from solutions with relative weight ratios of Gly and CA 80:20 (d), 90:10 (e), 98:2 (f).

## 2.2. Experimental Details of Single Crystal XRD

Single crystal X-ray diffraction (XRD) studies of Gly:CA (90:10) and Gly:CA (80:20) were performed in the Harbin Institute of Technology, China, by a Bruker D8 Venture setup (50 kV, 30 mA) at RT using Mo- $K_{\alpha}$  radiation, and Gly:CA (80:20) by Rigaku XtaLAB Synergy diffractometer at 100 K using Cu- $K_{\alpha}$  radiation (50 kV, 1 mA) in the Resource Center “X-ray Diffraction Methods” of St. Petersburg State University. The structures have been solved by the direct methods by means of the SHELX program [34] incorporated in the OLEX2 program package [35]. The carbon and nitrogen-bound H atoms were placed in calculated positions and were included in the refinement in the ‘riding’ model approximation. Empirical absorption correction was applied in CrysAlisPro program complex [CrysAlisPro, Version 1.171.36.32, Agilent Technologies Inc., Santa Clara, CA, USA] using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm [for Gly:CA (80:20)] and using the Bruker software SADABS-2016/2 [Bruker, 2016/2] [for Gly:CA (90:10)]. Supplementary crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC) (2194293–2194294) and can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (accessed on 8 April 2022). The drawings of the Gly:CA (90:10) and Gly:CA (80:20) crystal structures were made using the Vesta program [36].

## 2.3. Experimental Details of Powder XRD

To prepare the samples for powder XRD investigations, the grown crystals were grinded in a corundum mortar. Low-background holders in the form of polished single-crystal Si (119) plate were used to prepare powder samples for XRD measurements.



Powder XRD measurements were performed utilizing a D2 Phaser X-ray powder diffractometer (Bruker AXS, Karlsruhe, Germany) equipped with an X-ray tube with a copper anode and a Ni  $K_\beta$  filter (Cu- $K_\alpha$  radiation,  $\lambda = 1.54184 \text{ \AA}$ ). The XRD patterns were recorded in a symmetric scanning  $\theta$ - $2\theta$  mode using a semiconductor position-sensitive linear X-ray detector LYNXEYE (Bruker AXS, Karlsruhe, Germany). During the XRD measurements, temperature in sample chamber was  $313 \pm 1 \text{ K}$ . Additional XRD measurements of the powder samples mixed with internal XRD powder standard Si640f (NIST, Gaithersburg, MD, USA) were performed to win the angular corrections of the observed Bragg angles of the XRD reflections to zero shift and displacement.

After introducing the angular corrections to the Bragg angles  $2\theta_B$  of XRD reflections with attributed Miller indices  $hkl$ , at first stage of analysis, unit cell parameters of the crystalline phases were calculated using the program Celsiz [37], utilizing the least-square technique. Microstructural parameters (average size  $D$  of crystallites and absolute values of mean microstrain  $\epsilon_s$  in them) for crystalline phases were estimated from parameters of XRD reflections [Bragg angles  $2\theta_B$ , full width at half maximum  $FWHM_{obs}$ , maximum ( $I_{max}$ ) and integral ( $I_{int}$ ) intensities] by graphical methods of Williamson–Hall plot (WHP) [38] and size-strain plot (SSP) [39] adapted for pseudo-Voigt (pV) type of XRD reflections observed in the XRD patterns. All microstructure calculations [including the correction of the  $FWHM_{obs}$  to instrumental broadening for pV reflections (resulting in  $FWHM_{corr}$ )] were performed using the program SizeCr [40]. Detailed description of the formalism of microstructural calculations can be found elsewhere [40,41].

To confirm the reliability of the crystal structure model and the results of single-crystal XRD analysis, to obtain more accurate values of the unit cell and microstructure parameters, and to verify the single-phase nature of powder samples, the powder XRD patterns were studied by the Le Bail (LB) and Rietveld methods. The TOPAS program [42] was used for LB and Rietveld fittings. For LB fitting the XRD patterns, a structure model is not required, but only an approximate value of the unit cell parameters and symmetry space group knowledge [43]. Rietveld fitting is used for structure model refinement, including atomic coordinates and temperature parameters [44].

The XRD patterns of both samples are characterized by a noticeable influence of preferential orientation effects. Unlike the Rietveld method in the LB fitting, the influence of preferred orientation effects to XRD pattern is corrected automatically. When fitted by the Rietveld method, considering the effect of preferential orientation within the March–Dollase model [45] led to a decrease in the weighted profile factor  $R_{wp}$ , characterizing the quality of the fit by  $\sim 2.5$  and  $\sim 4$  times for  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20), respectively. Additional consideration of the remaining effects of preferential orientation in the framework of the 8th-order spherical harmonics model [46] led to a further decrease in  $R_{wp}$  by  $\sim 1\%$  for both samples.

Understated due to serial correlations [47], estimated standard deviations (e.s.d.s) of the refined parameters obtained using LB or Rietveld refinement were corrected by multiplying by the coefficient  $m_{e.s.d.}$  calculated using the RietESD program [48], based on the formalism developed in [47,49].

Other parameters of powder XRD measurements, WHP and SSP analysis, LB, and Rietveld fittings are the same as detailed in [31,41,50] and briefly discussed in Section S2 of the Supplementary Materials.

#### 2.4. Raman Scattering, FTIR, UV Vis Absorption, and Photoluminescence

Raman and micro-photoluminescence ( $\mu$ -PL) measurements in the Gly:CA single crystals were carried out using LabRAM HREvo UV-VIS-NIR-Open spectrometer (Horiba Jobin–Yvon, Lille, France) equipped with a confocal microscope and a silicon CCD cooled by liquid nitrogen. Polarized micro-Raman measurements were performed at RT, in the spectral range  $5\text{--}4000 \text{ cm}^{-1}$  at different backscattering geometries:  $-Z (XX)Z$ ,  $-Z (YY)Z$ , and  $-Z (XY)Z$ . Here, the Z-axis is oriented normally to the crystal surface (100), and X and Y are along  $c^*$ - and  $b$ -crystal axes, respectively. The line at  $\lambda = 532 \text{ nm}$  (2.33 eV) of Nd:YAG

laser (Torus, Laser Quantum, Inc., Edinburg, UK) was used as the excitation source. The laser power on the samples was as low as ~25–80  $\mu\text{W}$  with a spot size of ~1  $\mu\text{m}$  in diameter, to avoid sample heating. We used 1800 lines/mm grating and  $100\times$  ( $NA = 0.90$ ) objective lens to measure Raman spectra. In the low frequency spectral region, the Rayleigh line was suppressed using three BraggGrate notch filters (OptiGrate Corp., Oviedo, FL, USA) with an  $OD = 4$  and a spectral bandwidth  $<0.3$  nm.

The  $\mu\text{-PL}$  measurements were performed in microscope stage Linkam THMS600 (Linkam Sci. Inst. Ltd., Salfords, Surrey, UK). The line at  $\lambda = 325$  nm (2.81 eV) of HeCd laser (Plasma JSC, Ryazan, Russia) was used for continuous wave (CW) excitation. We used 600 lines/mm grating and a large working distance lens [Mitutoyo  $50\times$  UV ( $NA = 0.40$ )] with a spot size of ~2  $\mu\text{m}$  and power density of 6  $\text{kWt}/\text{cm}^{-2}$  on a sample was used to measure  $\mu\text{-PL}$ .

Measurements of the infrared (IR) absorption spectra (FTIR spectra) were performed using an IR-Fourier spectrophotometer IRPrestige-21 with an IR microscope AIM-8000 (Shimadzu Corp., Kyoto, Japan), both in the specular reflection mode and in the transmission mode, followed by the Kramers–Kronig transformation. The results were then converted to absorbance. The measured spectral range was from 650 to  $5000\text{ cm}^{-1}$ .

Optical absorption spectra of Gly:CA in the UV-visible (UV-Vis) spectral range were obtained using a UV-3600i Plus UV-Vis-NIR spectrophotometer (Shimadzu Corp., Kyoto, Japan) operating at RT in the wavelength range of 200–2000 nm. The test was conducted in reflection mode using an integrating sphere.  $\text{BaSO}_4$  was used as a reference sample.

### 3. Results and Discussion

#### 3.1. Single Crystal XRD Analysis

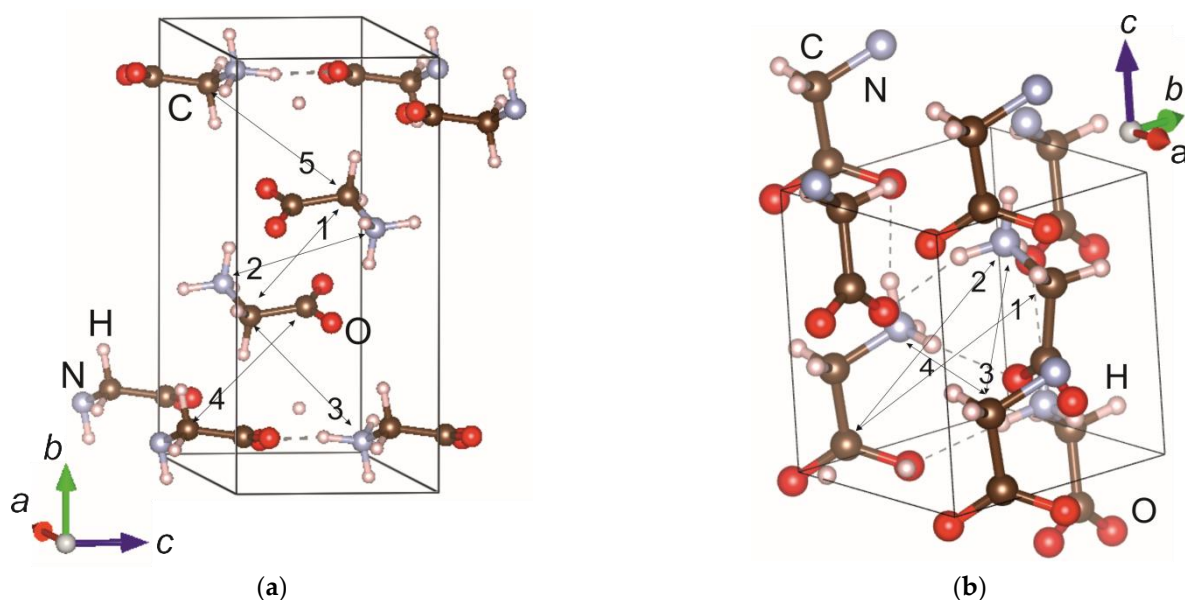
Single crystal XRD analysis indicates that the pyramid-like samples of Gly:CA (80:20) crystallize in a lattice typical to  $\gamma\text{-Gly}$  (space group  $P3_1$  (144)) ( $\gamma\text{-Gly:CA}$ ), and the plate-like crystals of Gly:CA (90:10) crystallize in  $\alpha\text{-Gly}$ -like structure (space group  $P2_1/n$  (14)) ( $\alpha\text{-Gly:CA}$ ) (Table 1). Structures of  $\alpha\text{-Gly:CA}$  (90:10) and  $\gamma\text{-Gly:CA}$  (80:20) are drawn in Figure 2 using the data of Table 1 and refined atomic coordinates (CCDC 2194293–2194294). Relative coordinates of atoms ( $x/a, y/b, z/c$ ), their isotropic temperature factors  $U$ , and atomic displacement parameters  $U^{ij}$  in  $\alpha\text{-Gly:CA}$  (90:10) and  $\gamma\text{-Gly:CA}$  (80:20) are presented in Supplementary Materials (Tables S1–S4). Figure S1 portrays the structure of glycine molecule in (a)  $\alpha\text{-Gly:CA}$  (90:10) and (b)  $\gamma\text{-Gly:CA}$  (80:20) with atoms represented by thermal ellipsoids by means of program ORTEP [51].

**Table 1.** Details of crystal data and structure refinement of  $\alpha\text{-Gly:CA}$  (90:10) and  $\gamma\text{-Gly:CA}$  (80:20) single crystals.

|                                                   | $\alpha\text{-Gly:CA}$ (90:10)    | $\gamma\text{-Gly:CA}$ (80:20)    |
|---------------------------------------------------|-----------------------------------|-----------------------------------|
| Chemical formula                                  | $\text{C}_2\text{H}_5\text{NO}_2$ | $\text{C}_2\text{H}_5\text{NO}_2$ |
| Formula weight, $D_a$                             | 75.07                             | 75.07                             |
| Space group                                       | $P2_1/n$ (14)                     | $P3_1$ (144)                      |
| $a$ , Å                                           | 5.1004 (5)                        | 6.9848 (3)                        |
| $b$ , Å                                           | 11.9664 (9)                       | 6.9848 (3)                        |
| $c$ , Å                                           | 5.4570 (5)                        | 5.4744 (2)                        |
| $\beta$ , °                                       | 111.714 (3)                       | 90                                |
| $V_{\text{cell}}$ , Å <sup>3</sup>                | 309.43 (5)                        | 231.30 (2)                        |
| $Z$                                               | 4                                 | 3                                 |
| $D_{\text{calc}}$ , $\text{g}\cdot\text{cm}^{-3}$ | 1.611                             | 1.617                             |
| $F(000)$                                          | 160.0                             | 120.0                             |
| $\mu$ , $\text{mm}^{-1}$                          | 0.143                             | 1.25                              |

Table 1. Cont.

|                                                            | $\alpha$ -Gly:CA (90:10)               | $\gamma$ -Gly:CA (80:20)               |
|------------------------------------------------------------|----------------------------------------|----------------------------------------|
| Radiation ( $\lambda$ , Å)                                 | Mo- $K_{\alpha}$ (0.71073)             | Cu- $K_{\alpha}$ (1.54184)             |
| $\Theta$ max, °                                            | 26.35                                  | 77.18                                  |
| $h, k, l$ max                                              | 6, 14, 6                               | 8, 8, 6                                |
| Reflections collected                                      | 3240                                   | 3120                                   |
| Independent reflections                                    | 629                                    | 645                                    |
| Data/restraints/parameters                                 | 629/0/47                               | 645/1/48                               |
| GOOF                                                       | 1.158                                  | 1.081                                  |
| Final $R$ indexes [Reflections $I \geq 2\sigma(I)$ ]       | $R_1 = 0.0345$ , $wR_2 = 0.1109$ [629] | $R_1 = 0.0299$ , $wR_2 = 0.0735$ [645] |
| Final $R$ indexes [Reflections all]                        | $R_1 = 0.0416$ , $wR_2 = 0.1173$ [538] | $R_1 = 0.0299$ , $wR_2 = 0.0735$ [645] |
| Largest difference peak/hole,<br>$e \cdot \text{\AA}^{-3}$ | 0.19/−0.19                             | 0.16/−0.20                             |
| Temperature of measurements, K                             | 298                                    | 100                                    |



**Figure 2.** Crystal structures of (a)  $\alpha$ -Gly:CA (90:10) and (b)  $\gamma$ -Gly:CA (80:20). Selected interatomic distances are marked in (a) for  $\alpha$ -Gly:CA (90:10) (1: 0.44 nm, 2: 0.53 nm, 3: 0.45 nm, 4: 0.49 nm, 5: 0.50 nm) and in (b) for  $\gamma$ -Gly:CA (80:20) (1: 0.60 nm, 2: 0.55 nm; 3: 0.54 nm; 4: 0.69 nm). Maximum size of flat CA molecule is  $\sim 0.5$  nm.

The crystal structures of all glycine phases are built from chains of glycine molecules linked by  $N1-H3 \cdots O2$  hydrogen bonds and directed along the crystal  $c$  axis of all polymorphic modifications. In  $\alpha$ -Gly, somewhat longer hydrogen bonds involving  $N1-H4 \cdots O1$  atoms form the second set of hydrogen bond chains running along the  $a$  crystal axis. These chains form a layer parallel to the (010) plane. The layers are arranged perpendicular to the  $b$  crystal axis. Due to the strong hydrogen bonds  $N1-H5 \cdots O1$ , a two-layer structure is formed, in which each pair of layers is connected to each other by weak hydrogen bonds of the  $C1-H1 \cdots O1$  and  $C1-H1 \cdots O2$ .

$\gamma$ -Glycine is trigonal, crystallizing in the chiral space groups  $P3_1$  (144). Its crystal structure does not consist of layers. Molecules form helices around the  $3_1$  screw-axis coinciding with the  $c$  crystal axis, successive molecules being linked by  $N1-H5 \cdots O2$  type hydrogen bonds. Hydrogen chains  $N1-H3 \cdots O2$  type along the  $c$  axis, like alpha-glycine,

are formed between each molecule and symmetry-equivalent molecules away along the helix, i.e., connected by one repetition of the lattice along the  $c$  crystal axis.

Analysis of single crystal XRD data indicates that the best refinement of the structure of  $\gamma$ -Gly:CA crystals can be achieved by considering twinning (twin components are related by screw axis  $3_1$ ). The crystals of  $\alpha$ -Gly:CA do not demonstrate twinning. Comparison with the literature data indicates (Table 2) that in centrosymmetric  $\alpha$ -Gly:CA (90:10), the unit cell volume  $V_{\text{cell}} = 309.43$  (5) Å<sup>3</sup> is little more than in pure  $\alpha$ -Gly [ $V_{\text{cell}} = 309.00$  (3) Å<sup>3</sup>] observed in [52], and smaller than  $V_{\text{cell}} = 310.10$  (4) Å<sup>3</sup> in [53]. In the magnitude of lattice parameters, CA doping manifests itself most clearly in decrease of  $c$  parameter and  $\beta$  angle in  $\alpha$ -Gly:CA and  $a$  and  $c$  parameters in  $\gamma$ -Gly:CA (Tables 2 and 3).

**Table 2.** Comparison of unit cell parameters  $a$ ,  $b$ ,  $c$ , angle  $\beta$ , and unit cell volume  $V_{\text{cell}}$  in  $\alpha$ -Gly:CA (90:10) and nominally pure  $\alpha$ -Gly crystals from [52,53].

|                                    | $\alpha$ -Gly:CA (90:10)<br>298 K | $\alpha$ -Gly [53]<br>294 K | $\alpha$ -Gly [52]<br>301 K |
|------------------------------------|-----------------------------------|-----------------------------|-----------------------------|
| $a$ , Å                            | 5.1004 (5)                        | 5.1047 (3)                  | 5.0999 (3)                  |
| $b$ , Å                            | 11.9664 (9)                       | 11.9720 (14)                | 11.9516 (6)                 |
| $c$ , Å                            | 5.4570 (5)                        | 5.4631 (3)                  | 5.4594 (3)                  |
| $\beta$ , °                        | 111.714 (3)                       | 111.740 (5)                 | 111.781 (2)                 |
| $V_{\text{cell}}$ , Å <sup>3</sup> | 309.43 (5)                        | 310.10 (4)                  | 309.00 (3)                  |

**Table 3.** Comparison of unit cell parameters  $a$ ,  $c$ , and unit cell volume  $V_{\text{cell}}$  in  $\gamma$ -Gly:CA (80:20) and nominally pure  $\gamma$ -Gly crystals from [53,54].

|                                    | $\gamma$ -Gly:CA<br>(80:20)<br>100 K | $\gamma$ -Gly [53]<br>150 K | $\gamma$ -Gly [54]<br>100 K | $\gamma$ -Gly [53]<br>294 K | $\gamma$ -Gly [54]<br>300 K |
|------------------------------------|--------------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $a$ , Å                            | 6.9848 (3)                           | 6.998 (16)                  | 6.9869 (1)                  | 7.0383 (7)                  | 7.0402 (1)                  |
| $c$ , Å                            | 5.4744 (2)                           | 5.4784 (18)                 | 5.4768 (1)                  | 5.4813 (8)                  | 5.4813 (1)                  |
| $V_{\text{cell}}$ , Å <sup>3</sup> | 231.30 (2)                           | 232.5 (1)                   | 231.540 (6)                 | 235.15 (3)                  | 235.280 (6)                 |

Comparison of bond lengths and angles of glycine molecules in CA-doped and pure  $\alpha$ - and  $\gamma$ -glycine crystals indicates that glycine zwitterions ( $^+\text{NH}_3\text{CH}_2\text{CO}_2^-$ ) in these crystals have close magnitudes of corresponding bond angles and bond lengths (Tables 4 and 5). Nevertheless, some small differences, which can be attributed to CA doping, may be indicated. CA doping of  $\alpha$ - and  $\gamma$ -Gly causes small increase of angle O1-C1-O2 and decrease of C2-C1-O1 that means the change of O1 atom position. However, doping does not influence other angles C2-C1-O2 and C1-C2-N1 in glycine molecules (Tables 4 and 5).

Thus, CA doping of  $\alpha$ - and  $\gamma$ -modifications of glycine single crystals does not lead to a change in symmetry and noticeable changes in the lattice parameters of the corresponding nominally pure glycine isomorphs. Like TGS:CA crystals [31], the incorporation of CA molecules into glycine crystals leads only to a slight modification of the unit cell parameters. In contrast to TGS:CA, the presence of twins is observed in noncentrosymmetric  $\gamma$ -Gly:CA crystals.

Note that both in TGS:CA and Gly:CA crystals, changes in bond angles and bond lengths were observed in glycine zwitterions. In TGS:CA, all bond angles in glycine zwitterions ( $^+\text{NH}_3\text{CH}_2\text{CO}_2^-$ ) are changed to bring it closer to the  $\text{N}^+\text{H}_3\text{CH}_2\text{COOH}$  [31] glycinium ion. Conversely, only a slight change in the position of O1 atoms in the carboxyl group and N atoms in the amino group of zwitterions is observed in Gly:CA, which indicates the formation of O...H-O and O...H-N types of hydrogen bonds between glycine zwitterions and croconic acid molecules.



**Table 4.** Bond angles and bond lengths C1–O1, C1–O2, C2–N1, and C1–C2 of glycine molecules in CA-doped and nominally pure  $\alpha$ -Gly crystals [52,53].

|                 | $\alpha$ -Gly:CA (90:10) | $\alpha$ -Gly [53] | $\alpha$ -Gly [52] |
|-----------------|--------------------------|--------------------|--------------------|
| bond angles, °  |                          |                    |                    |
| O1–C1–O2        | 125.86 (15)              | 125.62 (7)         | 125.45 (7)         |
| C2–C1–O1        | 116.69 (15)              | 116.93 (7)         | 117.16 (7)         |
| C2–C1–O2        | 117.44 (14)              | 117.44 (6)         | 117.38 (6)         |
| C1–C2–N1        | 111.78 (13)              | 111.70 (6)         | 111.83 (5)         |
| bond lengths, Å |                          |                    |                    |
| C1–O1           | 1.251 (2)                | 1.2549 (9)         | 1.2512 (10)        |
| C1–O2           | 1.247 (2)                | 1.2517 (9)         | 1.2480 (10)        |
| C2–N1           | 1.475 (2)                | 1.4777 (10)        | 1.4743 (8)         |
| C1–C2           | 1.526 (2)                | 1.5268 (9)         | 1.5252 (9)         |

**Table 5.** Bond angles and bond lengths C1–O1, C1–O2, C2–N1, and C1–C2 of glycine molecule in CA-doped and nominally pure  $\gamma$ -Gly crystals [53,54].

|                 | $\gamma$ -Gly:CA (80:20)<br>100K | $\gamma$ -Gly [53] 150 K | $\gamma$ -Gly [54]<br>100 K |
|-----------------|----------------------------------|--------------------------|-----------------------------|
| bond angles, °  |                                  |                          |                             |
| O1–C1–O2        | 126.0 (3)                        | 125.3 (2)                | 125.70 (7)                  |
| C2–C1–O1        | 116.4 (2)                        | 116.8 (2)                | 116.61 (7)                  |
| C2–C1–O2        | 117.6 (3)                        | 117.8 (2)                | 117.63 (6)                  |
| C1–C2–N1        | 111.6 (2)                        | 111.2 (2)                | 111.55 (6)                  |
| bond lengths, Å |                                  |                          |                             |
| C1–O1           | 1.260 (4)                        | 1.263 (3)                | 1.2572 (9)                  |
| C1–O2           | 1.248 (4)                        | 1.251 (3)                | 1.2487 (9)                  |
| C2–N1           | 1.479 (4)                        | 1.480 (3)                | 1.4719 (10)                 |
| C1–C2           | 1.524 (4)                        | 1.529 (3)                | 1.5249 (9)                  |

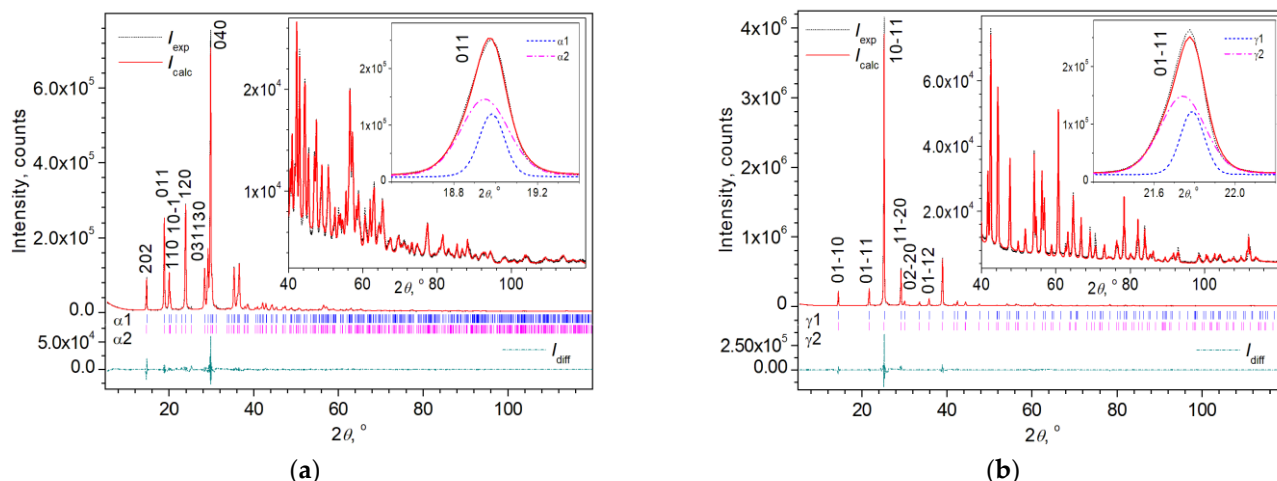
### 3.2. Powder XRD Analysis

Phase analysis has led to a conclusion that both the measured XRD patterns of  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20) contain the XRD reflections attributed to one phase expected according to preparation, namely,  $\alpha$ -Gly-like or  $\gamma$ -Gly-like phases (Table 1). However, a thorough inspection revealed that the reflections of the  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20) has an asymmetric shape, especially clearly seen for reflections non-overlapped with neighboring ones (see examples in small insets of Figure 3).

Recently, a similar asymmetric shape of powder XRD reflections of organic ferroelectric 2-methylbenzimidazole (MBI) has been successfully described in the framework of models of two or three crystalline phases with the same MBI structure but with slightly different unit cell parameters and differing microstructure parameters. The formation of the MBI modifications has been associated with penetration of solvent molecules (ethanol, acetone, deuterated acetone, or water) into the voids of the MBI crystal structure.

The structures of  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20) are also characterized by rather large pores with sizes of ~0.4 nm–0.6 nm (Figure 2). The CA molecules used during the synthesis of samples have a flat shape and a maximum size of ~0.5 nm. Based on these geometric observations, it can be assumed that CA molecules occupy the pores of structures during the sample synthesis. If CA molecules do not fill the lattice voids homogeneously,

but only some regions, then the filled lattice regions will stretch, forming modifications of the same structure with slightly larger lattice parameters. The average size of such regions with approximately the same content of CA molecules will determine the size of the crystallites of these different modifications. Simultaneously, due to the entry of CA molecules into the pores and the neighborhood of crystallites with slightly different lattice parameters, the presence of local microstrains in the crystallites of different modifications is possible.



**Figure 3.** Rietveld fit results for (a) α-Gly:CA (90:10) and (b) γ-Gly:CA (80:20). During the Rietveld fit the atomic coordinates of the phases were fixed to values determined in single-crystal investigation of this work and not refined. The Miller indices  $hkl$  and Miller–Bravais indices  $hkil$  of some selected reflections are indicated in (a) and (b), respectively. Large insets in (a,b) portray the quality of fitting the high  $2\theta$  angle regions of the XRD patterns in a larger scale. Small insets present examples of Rietveld fitting the asymmetric non-overlapping reflections.

To verify these assumptions, which appear reasonable, the WHP and SSP methods at first stage were used to perform a profile analysis of XRD reflections (XRD Line profile analysis, LPA) observed in XRD patterns, assuming two phases with close parameters of unit cells (correspondingly, α1 and α2 modifications or γ1 and γ2 ones for α-Gly:CA (90:10) and γ-Gly:CA (80:20) XRD patterns). To do this, each observed reflection was separated into two reflections with the same known Miller indices  $hkl$  [for α-Gly:CA (90:10)] or Miller–Bravais indices  $hkil$  [for γ-Gly:CA (80:20)], where possible (some reflections, especially in the high-angle region of  $2\theta > \sim 45^\circ$ , are highly overlapped, and it is difficult to extract them). The resulting WHP and SSP graphs are presented in the Figures S2 and S3 of Supplementary Materials. Table 6 presents the results of Celsiz and LPA calculations.

**Table 6.** Results of LPA (WHP and SSP) and LB and Rietveld fitting of the α-Gly:CA (90:10) and γ-Gly:CA (80:20) XRD powder patterns measured at  $313 \pm 1$  K.

| $a, \text{\AA}$<br>$b, \text{\AA}$                    | $c, \text{\AA}$<br>$\beta, ^\circ$                  | $V_{\text{cell}}, \text{\AA}^3$ | $D \text{ (nm)}$<br>$\varepsilon_s, \%$                       |
|-------------------------------------------------------|-----------------------------------------------------|---------------------------------|---------------------------------------------------------------|
| α-Gly:CA (90:10), LPA                                 |                                                     |                                 |                                                               |
| phase α1                                              |                                                     |                                 |                                                               |
| 5.1050 (16) <sup>a</sup><br>11.9771 (40) <sup>a</sup> | 5.4614 (17) <sup>a</sup><br>111.74 (2) <sup>a</sup> | 310.18 (18)                     | 52 (9)/78 (14) <sup>b</sup><br>0.07 (6)/0.16 (4) <sup>b</sup> |
| phase α2                                              |                                                     |                                 |                                                               |
| 5.1216 (20) <sup>a</sup><br>12.0064 (64) <sup>a</sup> | 5.4715 (22) <sup>a</sup><br>111.70 (3) <sup>a</sup> | 312.61 (25)                     | 44 (3)/54 (3) <sup>b</sup><br>0.06 (4)/0.14 (2) <sup>b</sup>  |
| α-Gly:CA (90:10), LB fitting                          |                                                     |                                 |                                                               |

Table 6. Cont.

| $a, \text{\AA}$<br>$b, \text{\AA}$                                                    | $c, \text{\AA}$<br>$\beta, ^\circ$                  | $V_{\text{cell}}, \text{\AA}^3$ | $D \text{ (nm)}$<br>$\varepsilon_s, \%$                  |
|---------------------------------------------------------------------------------------|-----------------------------------------------------|---------------------------------|----------------------------------------------------------|
| phase $\alpha 1$                                                                      |                                                     |                                 |                                                          |
| 5.1002 (10) <sup>c</sup><br>11.9709 (6) <sup>c</sup>                                  | 5.4613 (10) <sup>c</sup><br>111.68 (2) <sup>c</sup> | 309.85 (9)                      | 96 (4) <sup>c,d</sup><br>0.050 (6) <sup>c,d</sup>        |
| phase $\alpha 2$                                                                      |                                                     |                                 |                                                          |
| 5.1107 (5) <sup>c</sup><br>12.0102 (8) <sup>d</sup>                                   | 5.4694 (6) <sup>c</sup><br>111.70 (1) <sup>c</sup>  | 311.31 (5)                      | 37.4 (2) <sup>c,d</sup><br>0.11 (2) <sup>c,d</sup>       |
| $\alpha$ -Gly:CA (90:10), Rietveld fitting (without refinement of atomic coordinates) |                                                     |                                 |                                                          |
| phase $\alpha 1$                                                                      |                                                     |                                 |                                                          |
| 5.1000 (16) <sup>c</sup><br>11.9704 (8) <sup>c</sup>                                  | 5.4613 (9) <sup>c</sup><br>111.71 (2) <sup>c</sup>  | 399.76 (12)                     | 98 (5) <sup>c,d</sup><br>0.050 (6) <sup>c,d</sup>        |
| phase $\alpha 2$                                                                      |                                                     |                                 |                                                          |
| 5.1107 (5) <sup>c</sup><br>12.0102 (8) <sup>d</sup>                                   | 5.4694 (6) <sup>c</sup><br>111.70 (1) <sup>c</sup>  | 311.31 (5)                      | 38.4 (6) <sup>c,d</sup><br>0.11 (1) <sup>c,d</sup>       |
| $\alpha$ -Gly:CA (90:10), Rietveld fitting (with refinement of atomic coordinates)    |                                                     |                                 |                                                          |
| phase $\alpha 1$                                                                      |                                                     |                                 |                                                          |
| 5.0999 (10) <sup>c</sup><br>11.9701 (7) <sup>c</sup>                                  | 5.4613 (10) <sup>c</sup><br>111.71 (2) <sup>c</sup> | 309.74 (10)                     | 98 (5) <sup>c,d</sup><br>0.050 (6) <sup>c,d</sup>        |
| phase $\alpha 2$                                                                      |                                                     |                                 |                                                          |
| 5.1109 (7) <sup>c</sup><br>12.0102 (10) <sup>d</sup>                                  | 5.4684 (7) <sup>c</sup><br>111.69 (2) <sup>c</sup>  | 311.90 (8)                      | 38.9 (5) <sup>c,d</sup><br>0.12 (1) <sup>c,d</sup>       |
| $\gamma$ -Gly:CA (80:20), LPA                                                         |                                                     |                                 |                                                          |
| phase $\gamma 1$                                                                      |                                                     |                                 |                                                          |
| 7.0388 (6) <sup>a</sup><br>$a$                                                        | 5.4797 (9) <sup>a</sup><br>90                       | 235.12 (4)                      | 70 (12)/82 (7) <sup>b</sup><br>0/0.057 (16) <sup>b</sup> |
| phase $\gamma 2$                                                                      |                                                     |                                 |                                                          |
| 7.0541 (14) <sup>a</sup><br>$a$                                                       | 5.4890 (18) <sup>a</sup><br>90                      | 236.54 (9)                      | 48 (8)/48 (8) <sup>b</sup><br>0/0 <sup>b</sup>           |
| $\gamma$ -Gly:CA (80:20), LB fitting                                                  |                                                     |                                 |                                                          |
| phase $\gamma 1$                                                                      |                                                     |                                 |                                                          |
| 7.0404 (4) <sup>c</sup><br>$a$                                                        | 5.4838 (28) <sup>c</sup><br>90                      | 235.40 (12)                     | 92 (3) <sup>c,d</sup><br>0.044 (16) <sup>c,d</sup>       |
| phase $\gamma 2$                                                                      |                                                     |                                 |                                                          |
| 7.0600 (7) <sup>c</sup><br>$a$                                                        | 5.4903 (21) <sup>c</sup><br>90                      | 236.99 (10)                     | 35.7 (7) <sup>c,d</sup><br>0 <sup>c</sup>                |
| $\gamma$ -Gly:CA (80:20), Rietveld fitting (without refinement of atomic coordinates) |                                                     |                                 |                                                          |
| phase $\gamma 1$                                                                      |                                                     |                                 |                                                          |
| 7.0402 (5) <sup>c</sup><br>$a$                                                        | 5.4817 (35) <sup>c</sup><br>90                      | 235.30 (15)                     | 92 (4) <sup>c,d</sup><br>0.051 (17) <sup>c,d</sup>       |
| phase $\gamma 2$                                                                      |                                                     |                                 |                                                          |
| 7.0602 (9) <sup>c</sup><br>$a$                                                        | 5.4903 (9) <sup>c</sup><br>90                       | 237.01 (5)                      | 35.7 (9) <sup>c,d</sup><br>0 <sup>c</sup>                |

<sup>a</sup> calculated by program Celsiz. <sup>b</sup> calculated by WHP/SSP techniques using program SizeCr. <sup>c</sup> Parameters portrayed are corrected by multiplication of the e.s.d. values obtained in LB/Rietveld fitting refinement on  $m_{\text{e.s.d.}}$  factor (Table 7). <sup>d</sup>  $D = Lvol\_FWHM$  and  $\varepsilon_s (\%) = 2 \cdot e_0 \cdot 100\%$ , where  $Lvol\_FWHM$  and  $e_0$  are, respectively, crystallite size and microstrain parameters refined by TOPAS (see thorough explanation with examples in Refs. [40,41]).

**Table 7.** Agreement factors obtained in Rietveld and LB fitting (refinement), weight content *Wt* of crystalline phases p1 ( $\alpha 1$  or  $\gamma 1$ ) and p2 ( $\alpha 2$  or  $\gamma 2$ ) according to results of Rietveld fitting and the factor  $m_{e.s.d.}$  for correction of e.s.d.s of refined parameters calculated by RietESD.

| $R_{wp}, \%$<br>$R_p, \%$                                                             | $cR_{wp}, \%^a$<br>$cR_p, \%^a$ | $R_B, \% \text{ p1}$<br>$R_B, \% \text{ p2}$ | $Wt, wt.\% \text{ p1}$<br>$Wt, wt.\% \text{ p2}$ | $m_{e.s.d.}^a$ |
|---------------------------------------------------------------------------------------|---------------------------------|----------------------------------------------|--------------------------------------------------|----------------|
| $\alpha$ -Gly:CA (90:10), LB fitting                                                  |                                 |                                              |                                                  |                |
| 4.82<br>3.09                                                                          | 7.04<br>5.24                    | -<br>-                                       | -<br>-                                           | 5.05           |
| $\alpha$ -Gly:CA (90:10), Rietveld fitting (without refinement of atomic coordinates) |                                 |                                              |                                                  |                |
| 6.35<br>4.17                                                                          | 9.42<br>7.36                    | 0.98<br>1.13                                 | 24.4 (1) <sup>b</sup><br>75.6 (1) <sup>b</sup>   | 5.24           |
| $\alpha$ -Gly:CA (90:10), Rietveld fitting (with refinement of atomic coordinates)    |                                 |                                              |                                                  |                |
| 5.77<br>3.87                                                                          | 8.54<br>6.82                    | 0.71<br>0.58                                 | 23.4 (1) <sup>b</sup><br>76.6 (1) <sup>b</sup>   | 5.33           |
| $\gamma$ -Gly:CA (80:20), LB fitting                                                  |                                 |                                              |                                                  |                |
| 9.96<br>6.21                                                                          | 13.14<br>9.58                   | -<br>-                                       | -<br>-                                           | 6.97           |
| $\gamma$ -Gly:CA (80:20), Rietveld fitting (without refinement of atomic coordinates) |                                 |                                              |                                                  |                |
| 11.36<br>7.40                                                                         | 14.97<br>11.31                  | 1.94<br>2.92                                 | 33.2 (5) <sup>b</sup><br>66.8 (5) <sup>b</sup>   | 7.09           |

<sup>a</sup> Parameters calculated by program *RietESD* (see Supplementary Materials). <sup>b</sup> E.s.d. of *Wt* presented is corrected by multiplication of the e.s.d. value obtained in Rietveld fitting refinement on  $m_{e.s.d.}$  factor.

Based on the results of LPA, to perform the tasks set out in Section 2.3, the LB and Rietveld fittings of XRD patterns were performed in the next steps assuming the existence of two close-phase modifications in the samples ( $\alpha 1$  and  $\alpha 2$  in  $\alpha$ -Gly:CA (90:10) and  $\gamma 1$  and  $\gamma 2$  in  $\gamma$ -Gly:CA (80:20)).

Final graphic results of Rietveld fitting of the simulated XRD patterns to experimental ones (with atomic coordinates of the both phase modifications fixed to the values obtained in single-crystal refinement) for investigated powder samples are presented in Figure 3. The graphic results of LB fitting are provided in Figure S4 of Supplementary Materials.

Final values of agreement factors characterizing the quality of fitting simulated XRD patterns to experimental ones [weighted profile ( $R_{wp}$ ) and profile ( $R_p$ ) factors and their analogues after subtracting the background contribution ( $cR_{wp}$  and  $cR_p$ )] and the degree of correspondence of the structure model to the observed integral intensities of reflections attributed to crystalline phases (Bragg factors  $R_B$  for crystalline phases) for LB and Rietveld fitting are summarized in Table 7. Definitions of the agreement factors can be found, for example, in Ref. [55].

When only one phase is considered to exist, and all other things during fittings being equal, the weight profile factors  $R_{wp}$  increase by  $\sim 1.7$  times, and the profile factors  $R_p$  by more than 2 times compared to the factors provided in Table 7. In turn, the Bragg factor  $R_B$  increases by  $\sim 3$  times. Thus, the fitting of XRD patterns by LB and Rietveld methods unambiguously demonstrated that the assumption of only one phase does not allow us to describe XRD patterns and individual XRD reflections well enough. The powder samples contain at least two phases with a small difference in the unit cell parameters [ $\alpha 1$  and  $\alpha 2$  in  $\alpha$ -Gly:CA (90:10) and  $\gamma 1$  and  $\gamma 2$  in  $\gamma$ -Gly:CA (80:20)] at least.

As noted above, the coordinates of the atoms in the Rietveld fitting were not refined. In the case of  $\gamma$ -Gly:CA (80:20), in addition, a structural model was obtained by measuring a single crystal at 100 K, while the powder XRD pattern of this sample was taken at 313 K. Nevertheless, as can be observed from Figure 3 and Figure S4 (Supplementary Materials), the quality of powder XRD pattern fittings is quite high not only by the LB method, but also by the Rietveld method. The high quality of the fittings of powder XRD patterns indicates



the high quality of the results of the determination (refinement) of the structures of the samples performed on single crystals (which is expected), in addition to the absence of crystalline phases in the powder with the structures other than  $\alpha$ -Gly-like and  $\gamma$ -Gly-like in  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20), respectively.

An attempt to refine the atomic coordinates for modifications of the  $\alpha$ -Gly:CA (90:10) does not reveal a noticeable improvement in fitting quality (see Table 7 for agreement factors and Figure S5 of the Supplementary Materials). The values of the parameters of the unit cells of the modifications  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20) phases and the values of their microstructural parameters obtained in LB and Rietveld refinements practically coincide within one e.s.d. and are close (within two to three e.s.d.s) with values obtained independently by LPA methods (Table 6). Thus, for comparison with the results of single-crystal experiments (Tables 2 and 3), it is possible to consider the results with more precise values, for example, ones obtained in LB fitting (Table 6).

The similarity of the values of the parameters and volume of the unit cells of  $\alpha 1$  phase in powder and  $\alpha$ -Gly:CA (90:10) single-crystal phase with the values for pure  $\alpha$ -Gly according to the literature data [52,53] (cf. Tables 2 and 6) indicates that in the phase  $\alpha 1$  of powder and in the single-crystal  $\alpha$ -Gly:CA (90:10), likely only a small number of CA molecules have penetrated into the voids of the structures. The same conclusion can be drawn from the comparison with the literature data [53,54] for pure  $\gamma$ -Gly, apparently about the powder phase  $\gamma 1$  and the single-crystal  $\gamma$ -Gly:CA (80:20) (cf. RT and low-temperature data in Tables 3 and 6 for  $\gamma 1$  powder,  $\gamma$ -Gly:CA (80:20) single crystal and pure  $\gamma$ -Gly). Simultaneously, likely as a result of a larger number of CA molecules embedded in the pores of  $\alpha 2$  and  $\gamma 2$  modifications, their parameters and volumes of unit cells are noticeably larger than, respectively, in  $\alpha 1$  and  $\gamma 1$  (cf.  $V_{\text{cell}} = 311.31$  (5)  $\text{\AA}^3$  in  $\alpha 2$  and 236.99 (10)  $\text{\AA}^3$  in  $\gamma 2$ , in comparison to  $V_{\text{cell}} = 309.85$  (9)  $\text{\AA}^3$  in  $\alpha 1$  and 235.40 (12)  $\text{\AA}^3$  in  $\gamma 1$  (LB fit)).

According to the refinement by the Rietveld method, the weight content of phases  $\alpha 1$  and  $\gamma 1$  with a small number of embedded CA molecules in powders is significantly less than phases  $\alpha 2$  and  $\gamma 2$  with an increased volume due to the introduction of a higher number of CA molecules [correspondingly, ~24 wt.% and ~33 wt.% in  $\alpha 1$  and  $\gamma 1$  in comparison to ~76 wt.% and ~67 wt.% in  $\alpha 2$  and  $\gamma 2$  (Table 7)]. Nevertheless, as noted above, studies of single crystals have revealed precisely phases that are close in terms of unit cell parameters  $\alpha 1$  and  $\gamma 1$  (cf. Tables 1–3 and 6). Apparently, this fact can be explained by the results of the determination of microstructural parameters (Table 6). According to the results of LPA and refinements by LB and Rietveld methods, modifications  $\alpha 1$  and  $\gamma 1$  are characterized by large values of crystallite sizes in comparison with  $\alpha 2$  and  $\gamma 2$  (cf.  $D \sim 95$  nm in  $\alpha 1$  and  $\gamma 1$  and  $D \sim 40$  nm in  $\alpha 2$  and  $\gamma 2$ ). As a result, the reflections of  $\alpha 1$  and  $\gamma 1$  modifications are much narrower, and those of  $\alpha 2$  and  $\gamma 2$  phases are more blurred (see small insets in Figure 3a,b). It is likely that single crystals with unit cell parameters close to  $\alpha 2$  and  $\gamma 2$  were also characterized by more diffuse reflections and were rejected by quality when selected for single-crystal study.

Likely due to the embedding of CA molecules into structural pores and the neighborhood of crystallites of different modifications, microstrains are observed in the crystallites of  $\alpha 1$  and  $\gamma 1$  phases, which are approximately the same size ( $\epsilon_s \sim 0.05$  % (Table 6)). Simultaneously, in  $\alpha 2$  crystallites with a more expanded crystal lattice, the absolute value of the average microstrain increases to  $\epsilon_s \sim 0.10$ %. However, microstrains were not detected in the crystallites of modifications  $\gamma 2$  also characterized by an increased volume of the unit cell, which requires further investigation.

Thus, XRD studies of  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20) powders revealed the presence in them of at least two crystalline modifications with the same  $\alpha$ -Gly or  $\gamma$ -Gly type structure, respectively, but with slightly different unit cell parameters and noticeably different sizes of crystallites. The formation of two-phase modifications is associated with the embedding of different amounts of CA molecules into the pores of the  $\alpha$ -Gly and  $\gamma$ -Gly structures.

### 3.3. Raman and FTIR Spectroscopies

Polarized Raman spectra measured in Gly:CA crystals of both pyramidal (Figure 4a) and plate-like shapes (Figure 4b) are like those of nominally pure  $\alpha$ - and  $\gamma$ -Gly [56–58]. They consist of many lines, originated predominantly from intramolecular vibrations of different types. Analysis of the Raman and FTIR spectra makes it possible to ascertain the chemical structure and polymorphous modification of the molecular crystals studied. Tables 8 and 9 portray the position of the lines in the polarized Raman and FTIR absorption spectra in pyramidal [ $\gamma$ -Gly:CA (80:20)] and plate-like [ $\alpha$ -Gly:CA (90:10)] Gly:CA crystals, correspondingly. The positions of the lines in pyramidal Gly:CA crystals coincide with the positions of most lines in both nominally pure  $\gamma$ -Gly, and in plate-like  $\alpha$ -Gly:CA crystals [56–58]. The shifts in the positions of high-frequency spectral lines at high frequency in each pair of crystals ( $\alpha$ -Gly,  $\alpha$ -Gly:CA) and ( $\gamma$ -Gly,  $\gamma$ -Gly:CA) do not exceed several  $\text{cm}^{-1}$ . This indicates that the types and frequencies of molecular modes active in Raman spectra of  $\alpha$ - and  $\gamma$ -Gly doped with CA are close to those in pure Gly crystals. This is in agreement with the results of XRD analysis of Gly:CA single crystals and powders, which demonstrate very small changes in the crystal structure and position of atoms caused by doping with CA. Weak lines observed in  $\alpha$ -Gly:CA spectrum portrayed in Figure 4c by red arrows are absent in pure Gly crystals and can be attributed to CA ions [59] (see Table 9).

**Table 8.** Positions of lines ( $\nu$ ,  $\text{cm}^{-1}$ ) observed in polarized Raman and FTIR spectra of  $\gamma$ -Gly:CA (80:20) crystals and assignments of analogous lines in nominally pure  $\gamma$ -Gly from Ref. [58].

| Raman ( $\nu$ , $\text{cm}^{-1}$ ) |           |           | FTIR<br>( $\nu$ , $\text{cm}^{-1}$ ) | Assignments<br>[57]                  |
|------------------------------------|-----------|-----------|--------------------------------------|--------------------------------------|
| X(zz)X                             | X(yy)X    | X(yz)X    |                                      |                                      |
| -                                  | 3095.4 m  | -         | 3100 m                               | $\nu\text{NH (3)}\cdots\text{O (1)}$ |
| -                                  | 2999.1 s  | 2999.1 s  | -                                    | $\nu_a\text{CH}_2$                   |
| 2963.7 s                           | 2962.6 vs | 2964.8 m  | 2963 w                               | $\nu_s\text{CH}_2$                   |
| 2849.6 w                           | -         | -         | -                                    | -                                    |
| 2744.5 vw                          | -         | -         | -                                    | $\nu\text{NH (1)}\cdots\text{O (1)}$ |
| 2695.7 vw                          | -         | -         | -                                    | $\nu\text{NH (1)}\cdots\text{O (1)}$ |
| 2611.6 w                           | -         | -         | -                                    | $\nu\text{NH (1)}\cdots\text{O (1)}$ |
| -                                  | -         | -         | 1736 w                               | -                                    |
| -                                  | 1676.1 w  | -         | 1684m                                | -                                    |
| 1659.5 w                           | -         | -         | 1665 w                               | $\delta_a\text{NH}_3^+$              |
| -                                  | -         | -         | 1630 s                               | $\delta_a\text{NH}_3^+$              |
| -                                  | -         | -         | 1601 vs                              | $\nu_a\text{COO}^-$                  |
| -                                  | -         | 1589.8 w  | -                                    | -                                    |
| -                                  | 1576.5 m  | -         | -                                    | $\nu_a\text{COO}^-$ (?)              |
| -                                  | -         | -         | 1557 m                               | -                                    |
| -                                  | 1506.7 m  | -         | 1506 m                               | -                                    |
| -                                  | -         | 1502.3 vw | 1499 s                               | $\delta_s\text{NH}_3^+$              |
| 1483.5 vw                          | -         | -         | -                                    | $\delta_s\text{NH}_3^+$              |
| 1438.1 w                           | 1437 s    | 1440.3 m  | 1439 w                               | $\delta\text{CH}_2$                  |
| 1389.4 vw                          | 1393.8 s  | -         | 1398 m                               | $\nu_s\text{COO}^-$                  |
| -                                  | 1335.2 s  | -         | 1344 m                               | $\omega\text{CH}_2$                  |
| -                                  | -         | 1321.9 m  | 1321 w                               | $\tau\text{CH}_2$                    |
| -                                  | 1154.7 w  | 1156.9 vw | 1153 m                               | $\rho\text{NH}_3^+$                  |
| -                                  | 1135.9 m  | 1130.3 w  | -                                    | $\rho\text{NH}_3^+$                  |

Table 8. Cont.

| Raman ( $\nu$ , $\text{cm}^{-1}$ ) |           |           | FTIR<br>( $\nu$ , $\text{cm}^{-1}$ ) | Assignments<br>[57]    |
|------------------------------------|-----------|-----------|--------------------------------------|------------------------|
| X(zz)X                             | X(yy)X    | X(yz)X    |                                      |                        |
| -                                  | -         | -         | 1126 s                               | $\rho\text{NH}_3^+$    |
| -                                  | 1047.3 w  | 1048.4 m  | 1049 vw                              | $\nu_a\text{CCN}$      |
|                                    | 924.47 sh | 931.11 w  | 931.6 s                              | $\rho\text{CH}_2$      |
| 892.37 s                           | 892.37 s  | 892.37 w  | 889.2 m                              | $\nu\text{CC}$         |
| 749.55 vw                          | -         | -         | -                                    | -                      |
| 683.13 m                           | 688.67 vw | 687.56 w  | 692.4 m                              | $\sigma\text{COO}^-$   |
| -                                  | -         | -         | 667.37 m                             | -                      |
| 607.85 w                           | -         | 607.85 w  | -                                    | -                      |
| 560.24 vw                          | -         | 558.03 w  | -                                    | -                      |
| -                                  | -         | 517.07 w  | -                                    | $\omega\text{COO}^-$   |
| 502.68 s                           | -         | -         | -                                    | $\tau\text{COO}^-$     |
| -                                  | -         | 500.46 m  | -                                    | $\rho\text{COO}^-$     |
| 354.33 m                           | 354.33 w  | 359.86 w  | -                                    | $\rho\text{CCN}$       |
| -                                  | 213.,73 m | 215.94 w  | -                                    | -                      |
|                                    | -         | 171.66 sh | -                                    | $\omega$ or $\tau$ CCN |
| 174.98 w                           | -         | -         | -                                    | Lattice modes          |
| -                                  | 165.02 sh | -         | -                                    | -''-                   |
| -                                  | 149.52 s  | -         | -                                    | -''-                   |
| -                                  | -         | 138.45 s  | -                                    | -''-                   |
| -                                  | 127.38 sh | -         | -                                    | -''-                   |
| 108.56 vw                          | 101.92 m  | 103.02 m  | -                                    | -''-                   |
| 90.9 vw                            | 86.42 vs  | 87.528 m  | -                                    | -''-                   |

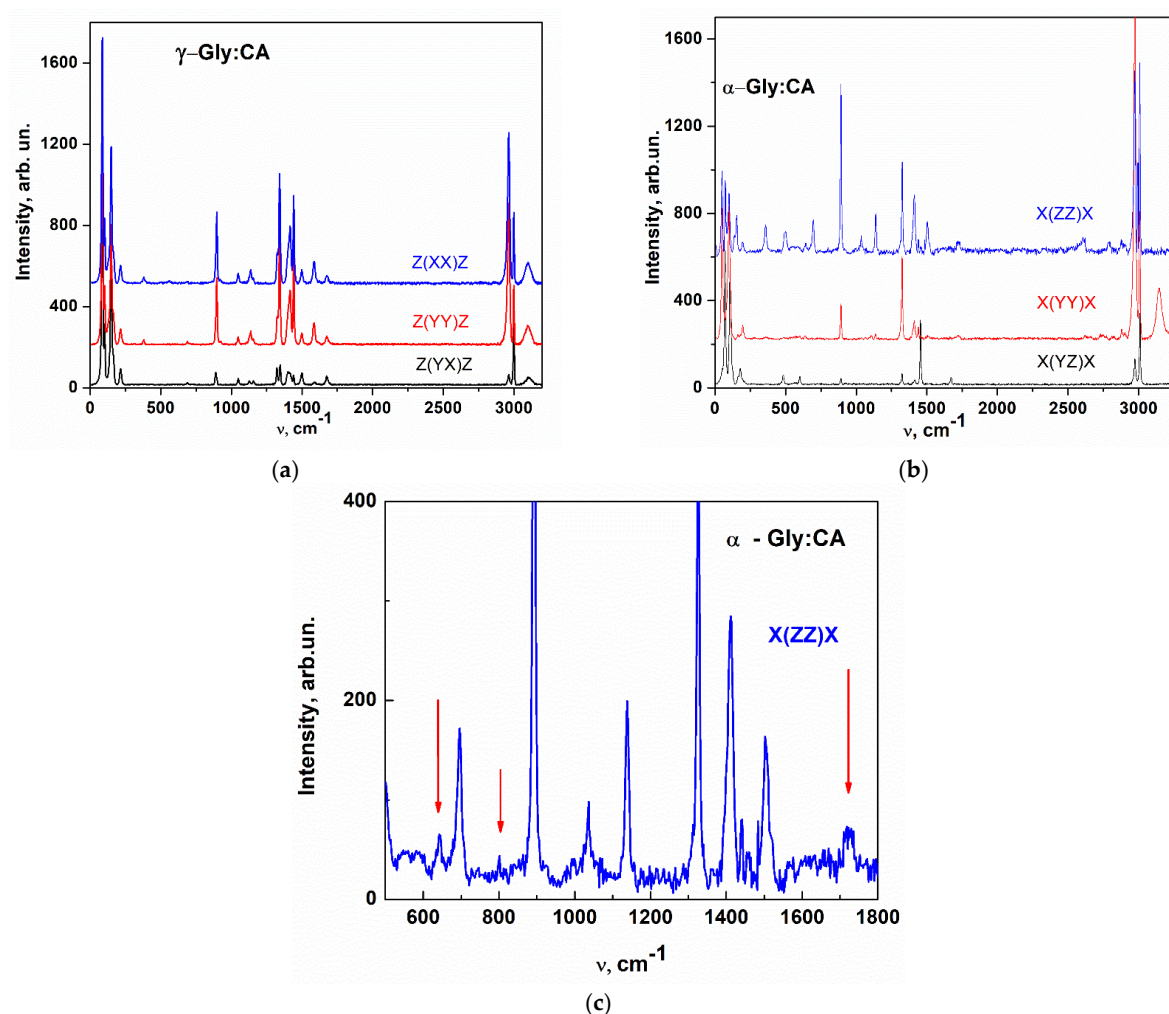
Table 9. Positions of lines ( $\nu$ ,  $\text{cm}^{-1}$ ) observed in polarized Raman and FTIR spectra of  $\alpha$ -Gly:CA (90:10) crystals and assignments of analogous lines in nominally pure  $\alpha$ -Gly from Ref. [58].

| X(ZZ)X  | X(YY)X  | X(YZ)X | FTIR        | Assignments [58]                                             |
|---------|---------|--------|-------------|--------------------------------------------------------------|
| -       | 3143 m  | -      | 3171 s<br>- | $\nu\text{NH}\cdots\text{O}$<br>$\nu\text{NH}\cdots\text{O}$ |
| 3008 vs | 3007 s  | 3009 s | 3005 m      | $\nu_a\text{CH}_2$                                           |
| 2972 vs | 2973 vs | 2973 s | 2974 m      | $\nu_s\text{CH}_2$                                           |
| -       | 2903 w  | -      | 2918 w      | $\nu\text{NH}\cdots\text{O}$                                 |
| 2883 vw | 2880 w  | -      | -           | -''-                                                         |
| -       | 2818 vw | -      | -           | -''-                                                         |
| 2787 vw | 2746 vw | -      | -           | -''-                                                         |
| -       | -       | -      | 2718 s      | -''-                                                         |
| 2608 vw | 2633 vw | -      | 2627 s      | -''-                                                         |
| -       | -       | -      | 2525 m      | -''-                                                         |
| -       | -       | -      | 2363 m      | -                                                            |
| 1723 vw | 1722 vw | -      | -           | CA [59]: $\nu$ (CO)                                          |
| -       | -       | 1673 m | 1647 vs     | $\delta_a\text{NH}_3^+$                                      |

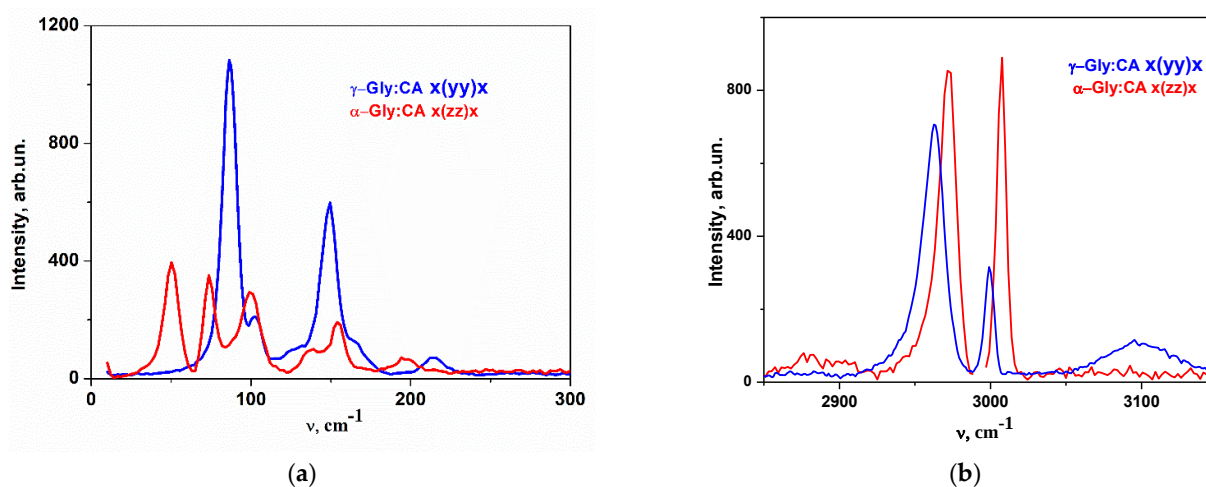
Table 9. Cont.

| X(ZZ)X  | X(YY)X   | X(YZ)X   | FTIR   | Assignments [58]              |
|---------|----------|----------|--------|-------------------------------|
| -       | -        | -        | 1611 s | $\delta_a\text{NH}_3^+$       |
| -       | -        | -        | 1555 m | $\nu_a\text{COO}^-$           |
| -       | -        | -        | 1541 m | -                             |
| 1502 m  | 1506 vw  | -        | 1508 m | $\delta_s\text{NH}_3^+$       |
| 1483 w  | -        | -        | 1474 w | $\delta_s\text{NH}_3^+$       |
| -       | -        | 1455 s   | 1458   | $\delta\text{CH}_2$           |
| -       | 1439 m   | -        | 1445 m | $\delta\text{CH}_2$           |
| 1411 s  | 1410 m   | 1416 w   | 1421 s | $\nu_s\text{COO}^-$           |
| -       | -        | -        | 1341 m | $\omega$ or $\tau\text{CH}_2$ |
| 1327 s  | 1325 s   | 1325 m   | 1314 m | $\tau\text{CH}_2$             |
| 1138 m  | 1137 w   | -        | 1134 w | $\rho\text{NH}_3^+$           |
| -       | 1106 w   | -        | 1115 w | $\rho\text{NH}_3^+$           |
| 1037 w  | -        | -        | 1034 w | $\nu_a\text{CCN}$             |
| -       | -        | -        | 914 s  | $\rho\text{CH}_2$             |
| -       | -        | -        | 897 m  | -                             |
| 892.8 s | 892.4 s  | 892.4 m  | -      | $\nu\text{CC}$                |
| 802 vw  | -        | -        | -      | CA [59]: $\delta$ (CO)        |
| 695.9 m | -        | -        | -      | $\sigma\text{COO}^-$          |
| 643 vw  | 639 vw   | -        | -      | CA [59]: Ring breath.         |
| -       | 600. vw  | 602.3 m  | -      | -                             |
| 496.9 w | -        | 483.9 m  | -      | $\rho\text{COO}^-$            |
| 357.2 m | -        | -        | -      | $\rho\text{CCN}$              |
| 196.3 m | 197.1 m  | -        | -      | Lattice modes                 |
| -       | -        | 178.3 m  | -      | -''-                          |
| -       | 161.7 w  | 163.9 sh | -      | -''-                          |
| 154 s   | -        | -        | -      | -''-                          |
| 139.2m  | -        | -        | -      | -''-                          |
| -       | -        | 107.5 s  | -      | -''-                          |
| 98.95 s | 99.71 s  | -        | -      | -''-                          |
| 73.54 s | 78.67 sh | -        | -      | -''-                          |
| -       | -        | 70.92 s  | -      | -''-                          |
| 50.26 s | 51 s     | 53.21 w  | -      | -''-                          |

The difference in polarized Raman spectra of  $\gamma$ - and  $\alpha$ -Gly is most evident in the position of strong lines in the region of low ( $0\text{--}300\text{ cm}^{-1}$ ) and high ( $2800\text{--}3100\text{ cm}^{-1}$ ) frequencies of the spectrum. This difference is clearly observed in the Raman spectra of pyramidal and plate-like Gly:CA crystals (Figure 4a,b). At high frequencies ( $2800\text{--}3100\text{ cm}^{-1}$ ) the stretching symmetric and antisymmetric vibrations of  $\text{CH}_2$  group have been observed in  $\alpha$ -Gly:CA at  $2973\text{ cm}^{-1}$  and  $3007\text{ cm}^{-1}$  and in  $\gamma$ -Gly:CA at  $2963\text{ cm}^{-1}$  and  $2999\text{ cm}^{-1}$  (Figure 5b), respectively, which corresponds to literature data related to pure  $\alpha$ - and  $\gamma$ -Gly [58]. At low frequencies ( $0\text{--}300\text{ cm}^{-1}$ ), positions of lines in  $\alpha$ - and  $\gamma$ -Gly:CA spectra are slightly shifted in compared to pure Gly crystals [56,57] (Tables S5 and S7 in Supplementary Materials), which may be attributed to CA doping.



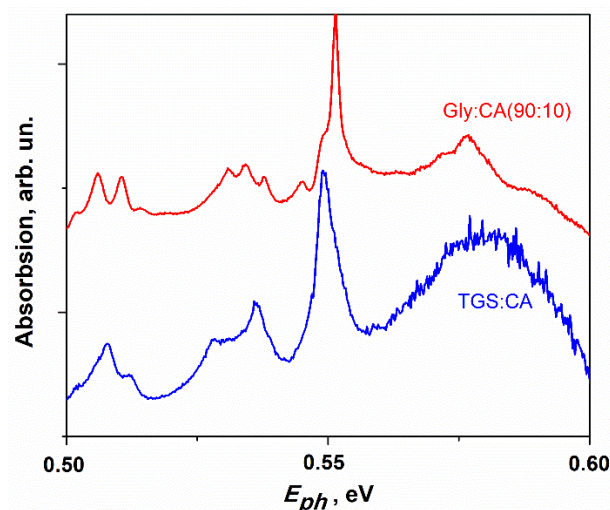
**Figure 4.** Polarized Raman spectra of pyramidal (a) and plate-like (b) Gly:CA crystals after subtracting the photoluminescence background. Fragment of the plate-like Gly:CA spectrum on an enlarged scale (c). For pyramidal crystals, the Z-axis is parallel to the polar axis (the height of the pyramid); for plate-like crystals, the Y-axis is parallel to the  $C_2$  axis. The red arrows in (c) indicate positions of lines observed in CA crystals.  $\lambda_{\text{exc}} = 532 \text{ nm}$ .



**Figure 5.** Comparison of Raman spectra of Gly:CA crystals of pyramidal (blue line) and plate-like (red line) shapes in low-energy (a) and high-energy (b) spectral regions.



As in the case of Raman spectra, a comparison of the FTIR absorption spectra of doped CA and nominally pure Gly indicates their close similarity (Tables 8 and 9). However, in the case of  $\alpha$ -Gly:CA (90:10) plates, additional lines in the photon energy range  $E_{ph} = 0.5\text{--}0.6\text{ eV}$  ( $4000\text{--}5000\text{ cm}^{-1}$ ) were observed in the FTIR absorption spectra measured in transmission geometry. Note that similar lines have been observed in the FTIR spectra of TGS crystals doped with CA [31] (Figure 6). No additional lines were observed in the reflection geometry, most likely due to their low intensity. Note that we did not measure FTIR absorption spectra of  $\gamma$ -Gly crystals in transmission geometry because of their pyramidal shape.



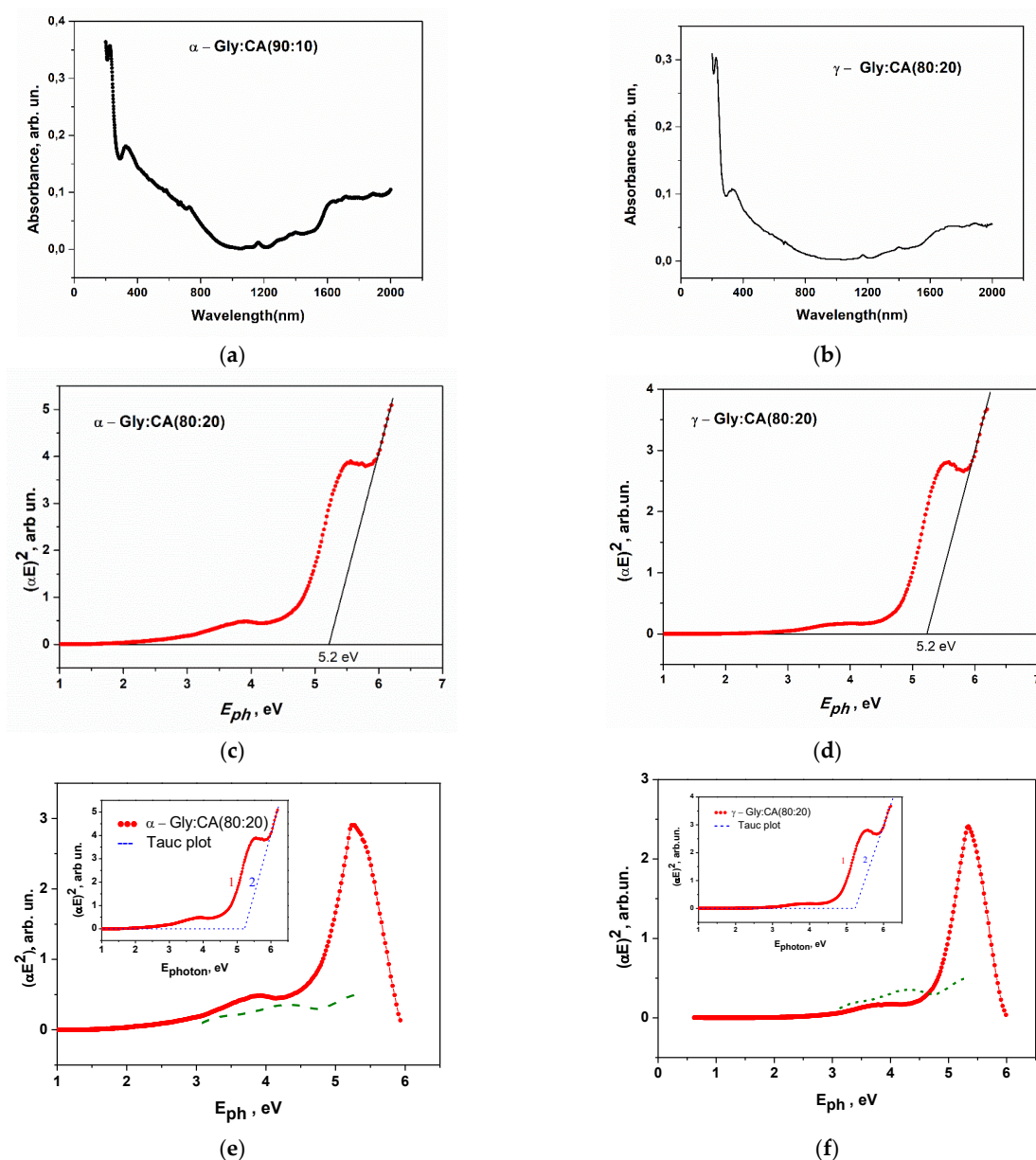
**Figure 6.** FTIR absorption spectra in spectral region  $E_{ph} = 0.5\text{--}0.6\text{ eV}$  in Gly:CA (90:10) measured in this work and in previously studied TGS:CA (90:10) (see text).

So, polarized Raman and FTIR absorption spectra of Gly:CA single crystals indicates that addition of croconic acid to the aqueous solution which was used to grow Gly:CA crystals does not significantly affect the polymorphic modification of the crystals grown. It has been established that  $\gamma$ -Gly forms pyramidal crystals, while  $\alpha$ -Gly forms plate-like crystals. The incorporation of CA molecules in a glycine crystal does not noticeably change the spectral positions of Raman lines in the high-energy region of the spectrum ( $2900\text{--}3100\text{ cm}^{-1}$ ), but leads to modest shift of several low-energy lines, which characterizes the effect of CA doping on the lattice vibration spectrum [32].

### 3.4. UV-Vis Absorption

RT absorption spectra of  $\alpha$ -Gly:CA (90:10) and  $\gamma$ -Gly:CA (80:20), are portrayed in Figure 7. Colorless  $\alpha$ - and  $\gamma$ -Gly crystals are transparent in wide spectral range. The energy band gaps of different polymorphic modifications of Gly crystals practically coincide and are about 5.1 eV [8,11,12]. Significant optical absorption is observed only for photons with energies  $E_{ph} > 5\text{ eV}$ , which manifests itself in a sharp increase of absorbance at  $\lambda < 240\text{ nm}$ . The doping of Gly with CA is accompanied by the appearance of absorption in the transparent region of pure Gly. This absorption manifests itself in the form of a structured long-wavelength tail adjacent to the edge of the fundamental absorption of a Gly crystal. The traits of the absorption are clearly observed when considering the absorption in Tauc coordinates ( $\alpha E_{ph}$ )<sup>2</sup>,  $E_{ph}$  (Figure 7c,d) (where  $\alpha$  is the absorption coefficient of the crystal). The shortest wavelength part of the absorption spectrum in region  $E_{ph} = (5.8\text{--}6.2)\text{ eV}$  in Figure 7c,d is well approximated by the linear dependence (solid black line), which can be regarded as the Tauc plot related to direct allowed interband transitions in crystals. The Tauc plot yields an estimation of the value of the optical bandgap as  $\sim 5.3\text{ eV}$ , which is close to the  $E_g$  value in pure Gly ( $\sim 5.1\text{ eV}$ ) (Figure 7c,d). Note that in Tauc coordinates, the shape of the absorption edge of undoped Gly is indeed well approximated by a straight line [8]. The presence of the additional absorption in the Gly:CA spectra (as compared with

undoped Gly) can be associated with electronic transitions involving defects in the Gly lattice induced by the introduction of CA molecules. The contribution of these transitions to the absorption spectrum can be estimated as the difference between the absorption spectrum of Gly:CA (line 1 in the insets in Figure 7e,f) and the fragment of its fundamental absorption spectrum modeled by the Tauc plot (line 2 in the insets in Figure 7e,f). The absorption spectra thus obtained are portrayed in Figure 7e,f, which includes at least two absorption bands with maxima at  $\sim 5.2$  and  $\sim 3.9$  eV. It should be noted that similar structure is observed in the absorption spectrum of CA solution in ethanol (olive line in Figure 7e,f) or in water [60]. In Gly:CA crystals the absorption bands can presumably be associated with the creation of excitons localized at the lattice defects, including impurity CA molecules or neighboring Gly ones.



**Figure 7.** Absorbance spectra of (a)  $\alpha$ -Gly:CA (90:10), (b)  $\gamma$ -Gly:CA (80:20), (c)  $\alpha$ -Gly:CA (90:10), and (d)  $\gamma$ -Gly:CA (80:20) in Tauc coordinates. (e,f) Change in the Gly crystal absorption caused by incorporating CA molecules into the Gly crystals. The olive lines represent the absorption spectrum of CA solution in ethanol [60]. The inset portrays the absorption spectra of doped and pure Gly crystals (see text).

Table 10 presents a comparison of the  $E_g$  values, and high and low frequency local bands in  $\alpha$ -Gly:CA (90:10),  $\gamma$ -Gly:CA (80:20), and TGS:CA (80:20) [31]. It is observed that CA doping results in practically the same changes of absorption spectra in these crystals.

**Table 10.** Energy gap  $E_g$ , eV, photon energy  $E_{ph}$  of high- and low-energy local bands and normalized amplitude of low energy band in absorption spectra of  $\alpha$ -Gly:CA (90:10),  $\gamma$ -Gly:CA (80:20) and TGS:CA (80:20) [31].

|                          | $E_g$ , eV | High Energy<br>Local band<br>$E_{ph}$ , eV | Low Energy<br>Local Band<br>$E_{ph}$ , eV | Normalized<br>Amplitude of Low<br>Energy Band |
|--------------------------|------------|--------------------------------------------|-------------------------------------------|-----------------------------------------------|
| $\alpha$ -Gly:CA (90:10) | 5.2        | 5.25                                       | 3.9                                       | 0.16                                          |
| $\gamma$ -Gly:CA (80:20) | 5.4        | 5.33                                       | 3.7                                       | 0.07                                          |
| TGS:CA (80:20)           | 5.2        | 5.39                                       | 3.9                                       | 0.2                                           |

Thus, doping of crystalline Gly with CA significantly affects the shape of the absorption edge of Gly, which manifests itself in smearing of the sharp absorption edge and the appearance of noticeable absorption at frequencies  $h\nu < E_g$ . Note that the same changes of absorption spectrum have been observed earlier in CA-doped triglycine sulfate crystals [31].

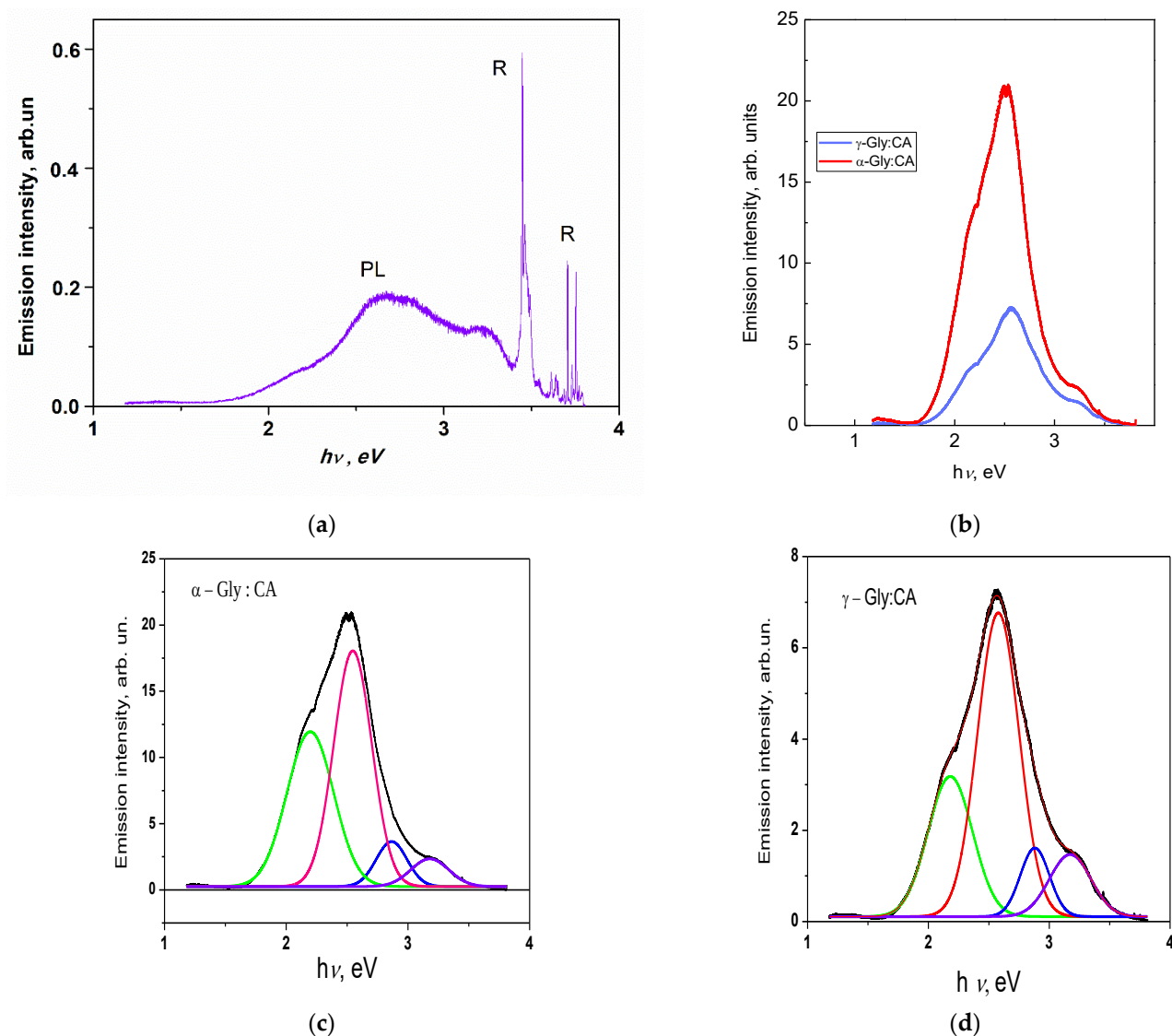
### 3.5. Photoluminescence

The photoluminescence (PL) of “pure” glycine crystals is very weak. As a result, in the emission spectrum of “pure”  $\gamma$ -Gly narrow Raman lines are clearly observed, whose intensity is comparable to that of the luminescence band (Figure 8a). Like pure glycine, solid croconic acid is also practically non-luminescent [61]. However, doping glycine crystals with croconic acid leads to a dramatic increase in the emission intensity, while the intensity of Raman scattering does not change (Figure 8b). Thus, the relatively bright luminescence of  $\gamma$ -Gly:CA is a distinctive characteristic of the doped crystals. A similar situation also occurs in the case of  $\alpha$ - Gly:CA.

The RT PL spectra of  $\alpha$ - and  $\gamma$ -Gly:CA crystals excited by light with  $\lambda_{exc} = 325$  nm are portrayed in Figure 8b. The spectra of both  $\gamma$ - and  $\alpha$ -modifications consist of broad structured emission bands with their maxima at  $\sim 2.50$  eV ( $\gamma$ -Gly:CA) and  $\sim 2.56$  eV ( $\alpha$ -Gly:CA), respectively. Comparison of the PL spectra of pure and doped Gly crystals (Figure 8) portrays that the shapes of the PL bands are practically identical, but doping Gly with croconic acid leads mainly to a dramatic increase in the PL intensity. Considering that the band gap of  $\gamma$ -glycine crystals is about 5 eV [8,11–13] the optical electron transitions responsible for the emission involve localized electron states whose energy levels are located within the crystal band gap.

Figure 8c,d portrays the decomposition of the emission band profile into four Gaussian components both in the case of  $\alpha$ -Gly:CA and  $\gamma$ -Gly:CA. The positions of the Gaussian components and their relative intensity in the PL spectra of  $\alpha$ -Gly:CA (90:10),  $\gamma$ -Gly:CA (80:20), and TGS:CA (90:10) [31] are presented in Table 11. The observed emission-band structure implies the presence of at least four different emitting centers that contribute to the emission of Gly:CA crystals. Note that the expansion of the TGS:CA (90:10) PL spectrum in terms of the Gaussian component presented in our previous paper [31] contains only three components. Here, we present the results of more accurate calculations that include four Gaussian components which provide a better fit. Both in Gly:CA crystals and in TGS:CA crystals, the positions and normalized intensities of the Gaussian components in both Gly:CA and TGS:CA crystals are close, which demonstrates that in all the crystals compared the PL originates from the same emission centres. The similar PL behavior in CA-doped Gly and TGS crystals clearly indicates that the appearance of PL is not associated with the  $SO_4$  groups, which are present in TGS but absent in Gly crystals. The PL is probably the result of the interaction of CA with glycine ions and, most likely, with glycine

zwitterions, since, as XRD phase analysis demonstrates, the structural parameters of these ions are affected by CA doping.



**Figure 8.** (a) Emission spectrum of “pure”  $\gamma$ -glycine with a small admixture of citric acid. Here, R labels the Raman lines. (b) Emission spectra of  $\gamma$ - and  $\alpha$ -glycine crystals doped with croconic acid. (c) Decomposition of the  $\alpha$ -Gly:CA emission band profile into four Gaussian components.  $h\nu_{\text{exc}} = 3.8$  eV.  $T = 300$  K. (d) Decomposition of the  $\gamma$ -Gly:CA emission band profile into four Gaussian components. The Gaussian components in (c,d) are shown by different colors.

**Table 11.** Resonance photon energies  $E_{\text{ph}}$ , eV, normalized intensity  $A_i/A_2$  obtained after decomposition of PL spectra in  $\alpha$ -Gly:CA,  $\gamma$ -Gly:CA and TGS:CA in four Gauss components.

| Band, $i$ | $\alpha$ -Gly:CA     |           | $\gamma$ -Gly:CA     |           | TGS:CA               |           |
|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|
|           | $E_{\text{ph}}$ , eV | $A_i/A_2$ | $E_{\text{ph}}$ , eV | $A_i/A_2$ | $E_{\text{ph}}$ , eV | $A_i/A_2$ |
| 1         | 2.20                 | 0.66      | 2.18                 | 0.47      | 2.20                 | 0.59      |
| 2         | 2.54                 | 1         | 2.57                 | 1         | 2.57                 | 1         |
| 3         | 2.86                 | 0.20      | 2.88                 | 0.24      | 2.86                 | 0.33      |
| 4         | 3.18                 | 0.13      | 3.17                 | 0.22      | 3.19                 | 0.22      |



From Table 11 we observe that the normalized intensities of Gauss components may depend on crystal symmetry because bands 3 and 4 in non-centrosymmetric  $\gamma$ -Gly, and TGS:CA are more intensive than in centrosymmetric  $\alpha$ -Gly:CA and band 1 has higher amplitude in  $\alpha$ -Gly:CA.

Although the specific structure of these centers is currently not clear, it can be assumed that they include molecules of both glycine and croconic acid (glycine and CA crystals are not luminescent by themselves). The presence of an analogous emission band in the luminescence spectrum of “pure”  $\gamma$ -Gly (Figure 8a) with a small admixture of citric acid demonstrates that not only CA but also other organic acids can promote the formation of emitting centers (glycine lattice defects) with a similar structure of radiative transitions.

#### 4. Conclusions

Crystals of  $\alpha$ - and  $\gamma$ -glycine doped with croconic acid were grown from aqueous solutions of glycine and croconic acid.  $\alpha$ -Gly crystals grown from a solution with a relative weight content Gly and CA of 90:10 have a plate shape. Pyramid-shaped  $\gamma$ -Gly crystals were obtained from a solution with a relative weight content of 98:2 and 80:20. A study of the structural and optical properties of the grown crystals has been performed. The study indicates that the crystal symmetry and morphology of CA-doped-doped glycine single crystals grown from aqueous solutions with different components weight ratios correspond well to well-known  $\alpha$ - and  $\gamma$ -isomorphs of nominally pure glycine. Incorporation of CA molecules in the host glycine crystal structures does not change remarkably the parameters of the unit cells, but results in small changes of unit cell volumes, and bond angles and lengths of glycine zwitterions.

In many aspects, this situation is quite similar to that observed in CA-doped TGS single crystals [31]. CA doping both Gly and TGS crystals does not significantly change the frequencies of molecular vibrations in Raman and FTIR spectra. Also, it does not remarkably influence the magnitude of forbidden gap  $E_g$ , caused by direct allowed electronic transitions.

The most significant changes caused by CA doping glycine (Gly:CA), as in the case TGS crystals, are associated with absorption and photoluminescence spectra. In the UV Vis region CA doping results in appearance of a strong absorption band caused by local electronic transitions near the band gap ( $E_{ph} \approx 5.2$ – $5.4$  eV), and a broad band of lower intensity with a maximum in the region of  $E_{ph} \approx 3.7$ – $3.9$  eV. Weak absorption bands were detected by FTIR in TGS:CA and Gly:CA in the region of  $E_{ph} \approx 0.5$ – $0.7$  eV.

Strong PL spectra in  $\alpha$ -,  $\gamma$ -Gly:CA, and TGS:CA crystals demonstrate the contributions of four emission centers emitting photons of close energies ( $\sim 2.2$  eV, 2.57 eV, 2.86 eV, 3.18 eV) and intensity ratios. It can be assumed that the appearance of these centers is due to the incorporation of small CA ions into the pores of the host crystal structure and the formation of hydrogen bonds between the CA molecule and glycine zwitterions.

In  $\alpha$ - and  $\gamma$ -Gly:CA, in contrast to TGS:CA, different phases (regions) with a crystal structure of the same symmetry but slightly different unit cell parameters arising from the inhomogeneous doping distribution of the CA molecule in the host crystal were revealed by powder X-ray diffraction methods. The presence of twins in non-centrosymmetric  $\gamma$ -Gly:CA was detected using single-crystal XRD. These crystal structure details do not appear in optical spectroscopy experiments due to the integral nature of these methods.



**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12101342/s1>. Table S1: Results of refinement of the  $\alpha$ -Gly:CA (90:10) structure (space group  $P2_1/n$  (14)) using single crystal XRD data. Table S2: Atomic displacement parameters for the  $\alpha$ -Gly:CA (90:10) ( $\text{\AA}^2$ ). Table S3: Results of refinement of the  $\gamma$ -Gly:CA (80:20) structure (space group  $P3_1$  (N 144)) using single crystal XRD data. Table S4: Atomic displacement parameters for the  $\gamma$ -Gly:CA (80:20) ( $\text{\AA}^2$ ). Figure S1: Structures of (a)  $\alpha$ -Gly:CA (90:10) and (b)  $\gamma$ -Gly:CA (80:20) with atoms represented by thermal ellipsoids by means of program ORTEP using, correspondingly, the data presented in Tables S1–S4. Figure S2: (a), (c) WHP and (b), (d), (f) SSP of  $\alpha$ 1 and  $\alpha$ 2 modifications of  $\alpha$ -Gly. Figure S3: (a), (c) WHP and (b), (d), (f) SSP of  $\gamma$ 1 and  $\gamma$ 2 modifications of  $\gamma$ -Gly. Figure S4: LB fit results for (a)  $\alpha$ -Gly:CA (90:10 and (b)  $\gamma$ -Gly:CA (80:20). Figure S5: Rietveld fit results for  $\alpha$ -Gly:CA (90:10). Table S5: Low frequency intermolecular modes and symmetry modes in Gly:CA plate in different experimental geometries, and in nominally pure  $\alpha$ -Gly [5]. Table S6: High frequency intramolecular modes in Gly:CA plate in different experimental geometries, and in nominally pure  $\alpha$ -Gly [6]. Table S7: Low frequency intermolecular modes in Gly:CA pyramid in different experimental geometries, and in nominally pure  $\gamma$ - Gly [7]. Table S8. High frequency intramolecular modes in Gly:CA pyramid.

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