Raman scattering and luminescence in single crystals of the amino acid glycine C$_2$H$_5$NO$_2$ with an admixture of croconic acid C$_5$H$_2$O$_5$

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Abstract. Single crystals of the amino acid glycine (Gly) C$_2$H$_5$NO$_2$ doped with croconic acid (CA) C$_5$H$_2$O$_5$ were synthesized by evaporation from an aqueous solution. The crystals grow in the form of hexagonal pyramids or thin plates. Analysis of polarized Raman scattering spectra (excitation wavelength of 532 nm) measured at room temperatures showed that crystals in the form of pyramids corresponded to $\gamma$-polymorph ($\gamma$-Gly), and crystals in the form of plates to $\alpha$-polymorph of glycine ($\alpha$ - Gly). The presence of croconic acid molecules in the crystals is confirmed by the change in their color from white in pure Gly crystals to light or dark yellow, characteristic of CA crystals, as well as the presence of weak lines corresponding to CA in the Raman spectra. In single crystals of both Gly:CA polymorphs, strong green luminescence significantly exceeding the intensity of Raman scattering is observed in the range 400 - 700 nm with a maximum at 510 nm (2.44 eV) upon excitation at $\lambda$= 325 nm.

1. Introduction
Currently, there is an active search and study of new organic ecological multifunctional materials with ferroelectric, piezoelectric, nonlinear optical and luminescent properties. [1, 2]. Non-centrosymmetric organic crystals attract attention due to their optical transparency in a wide wavelength range, optical stability, the presence of the piezoelectric effect, and also the ability to grow bulk high-quality crystals by relatively simple methods. The presented work is devoted to the synthesis and optical studies of single crystals of the protein amino acid glycine (Gly) C$_2$H$_5$NO$_2$ doped with croconic acid (CA) C$_5$H$_2$O$_5$.

Crystallization of glycine, NH$_2$-CH$_2$-COOH, is characterized by polymorphism. At atmospheric pressure, Gly crystallizes in the form of $\alpha$-, $\beta$- or $\gamma$-modifications. $\alpha$-glycine has a monoclinic centrosymmetric crystal structure (space group P2$_1$/n), $\beta$- and $\gamma$- glycine crystallize in non-centrosymmetric structure of monoclinic (sp.gr. P2$_1$) and trigonal (sp.gr. P3$_1$) symmetry, respectively, [3]. $\alpha$-Gly crystallizes from aqueous solution with pH = 2.5 - 10. $\gamma$-Gly crystallizes from aqueous solution with pH < 2.5, when an acid is added to water, or for pH > 10 with adding to aqueous solution some compounds containing alkaline monovalent ions [4]. $\beta$-Gly is not stable and can transform in more stable $\alpha$-Gly or $\gamma$-Gly. $\gamma$-Gly transforms in $\alpha$-Gly at T $\approx$ 460 K [5].

Non-centrosymmetric $\gamma$-Gly crystals are characterized by high optical transparency in wide spectral range (band gap ~ 5 eV, $\lambda_{gap}$ $\approx$ 230 nm), by values of nonlinear optical (NLO) efficiency two times higher than in KDP [5-9], by piezoelectric and pyroelectric effect with corresponding coefficients $d_{33}$ ~ 8 pC/N [10, 11] and $p$ $\sim$13 $\mu$C/m$^2$K [12]. For increase of stability and second harmonic generation...
(SHG) efficiency $\gamma$-Gly crystals have been grown from aqueous solution with adding of different substances such as sodium hydroxide, sodium bromide, potassium fluoride, potassium nitrate, lithium acetate, and other, etc [13–15].

CA molecule C$_5$H$_2$O$_5$ belongs to a series of planar monocyclic C$_n$H$_2$O$_n$ oxocarbon acids. It has highly symmetric ($D_{5h}$) plane topology and large value of molecular dipole momentum $d \sim (9–10)$ D [16]. CA molecule is small and may be incorporated into the host lattice as an impurity in a wide concentration range.

CA crystals with orthorhombic symmetry and the space group Pca2$_1$ are above room temperature ferroelectrics with the highest spontaneous polarization value among organic crystals $P_s = 30 \mu$C/cm$^2$ at room temperature [16]. This value exceeds the value of spontaneous polarization in the classic inorganic ferroelectric barium titanate. CA crystals are also characterized by high values of NLO parameters [17]. In spite of the fact that croconic crystals does not exhibit photoluminescence, an incorporation of CA molecules in the polymer [Ag$_4$(C$_5$O$_5$)$_2$(H$_2$O)$_2$]$_n$ results in green luminescence under the excitation of 380 nm light [18].

The aim of this work was synthesis of Gly:CA single crystals by means of evaporation from aqueous solution of glycine and croconic acid and study their optical properties (Raman scattering and photoluminescence).

2. Experimental

Gly:CA crystals were grown from a saturated aqueous solution of aminoacetic acid powder ($\alpha$-glycine) and croconic acid crystals. CA crystals (Fig.1a) were obtained by recrystallization of the Alfa Aesar reagent (CA 98%) according to the procedure described in [19]. CA crystals have a yellow colour (Figure 1a). The yellow colour of Gly:CA crystals grown was found to be dependent on the concentration of CA in the solution. The relative weight content of the Gly and CA components in solution was 80:20 (type 1), 90:10 (type 2) and 98:2 (type 3). Images of the synthesized crystals are shown in figure 1c-e. Gly:CA crystals grown from solution of type 1, 3 have a pyramidal shape with a hexagonal base (Figures 1c and 1e), and from type 2 solution a shape of plates (Figure 1d). Colorless "pure" $\gamma$-Gly crystals were grown from water solution with adding 5% of citric acid C$_6$H$_8$O$_7$ (Figure 1b) and may contain a small admixture of the acid.

**Figure 1.** Images of (a) CA crystals after recrystallization, (b) $\gamma$-Gly crystal grown from water solution with adding 5% of citric acid C$_6$H$_8$O$_7$, (c-d) Gly: CA crystals grown from solution with different relative weight relation of Gly and CA c) type 1, d) type 2, e) type 3.
The optical properties of the Gly:CA single crystals samples were studied using T64000 spectrometer (Horiba Jobin–Yvon, France) equipped with a confocal microscope and a silicon CCD cooled by liquid nitrogen. Polarized micro-Raman measurements were performed at room temperature, in the spectral range 5–4000 cm⁻¹ at different backscattering geometries: -Z(XX)Z, -Z(YY)Z, and -Z(XY)Z. Here, Z-axis is oriented normally to the crystal surface (100), and X and Y are along a*- and b-crystal axes, respectively. The line at 𝜆 = 532 nm (2.33 eV) of Nd:YAG laser (Torus, Laser Quantum, Inc., UK) was used as the excitation source. The laser power on the samples was as low as ~25–80 µW with a spot size of ~1 µm in diameter, to avoid sample heating. We used 1800 lines/mm grating and 100x (NA = 0.90) objective lens to measure Raman spectra. In the low frequency spectral region, the Rayleigh line was suppressed using three BragGrate notch filters (OptiGrate Corp., USA) with an OD=4 and a spectral bandwidth <0.3 nm. The micro-photoluminescence (µ-PL) measurements in the temperature range from 80 to 300K were carried out in a temperature controlled microscope stage Linkam THMS600 (Linkam Sci. Inst. Ltd., UK). The line at 𝜆 = 325 nm (2.81 eV) of HeCd laser (Plasma, Russia) was used for cw excitation. We used 600 lines/mm grating and a large working distance lens (Mitutoyo 50x UV (NA = 0.40)) with a spot size of ~2 µm and power density of 6 kWt/cm² on a sample was used to measure µ-PL.

3. Raman scattering
Polarized Raman spectra measured in Gly:CA crystals of pyramidal (Figure 2a) and plate-like (Figure 2b) shapes, similar to the spectra of α- and γ- Gly [20-22], consist of a large number of lines, originated from internal molecular vibrations of various nature, which makes it possible to use Raman spectroscopy to check their molecular structure and polymorph modification. The position of the lines in Gly:CA crystals of a pyramidal shape coincides well with position of most lines in γ- Gly [22], and in the plate-like Gly:CA crystals with position of most lines in α- Gly [20-22]. The difference in polarized Raman spectra of γ- and α- Gly is most evident in the position of strong lines in the region of low (0-300 cm⁻¹) and high (2800–3100 cm⁻¹) frequencies of the spectrum. This difference is clearly seen in the Raman spectra of pyramidal and plate-like Gly:CA crystals (Figure 3 a,b). The position of lines in Gly:CA crystals shown in figure 3, and the corresponding lines in α- and γ- Gly crystals, known from the literature, are presented in tables 1-4.

![Figure 2](image-url) Polarized Raman spectra of Gly:CA crystals with pyramidal (a) and plate-like (b) shapes after subtracting the photoluminescence background at excitation 𝜆 = 532 nm. Z axis at (a) is parallel to the polar axis (the height of the pyramid). Y axis at (b) is parallel to C₂ axis. The red arrows in inset indicate positions of lines observed in CA crystals [23].
**Figure 3.** 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, showing their various polymorphic modifications.

**Table 1.** Low frequency intermolecular modes in Gly:CA plate.

| Mode | Symbol | α-Gly [21] | Sym. |
|------|--------|------------|------|
| X(ZZ)X | X(YY)X | X(YZ)X | |
| 1 | 50 s | 51 s | 53 w | 52 | Ag |
| 2 | 99 s | 100 s | 110 | Ag |
| 3 | 154 s | 178 m | 178 | Bg |
| 4 | 196 m | 197 m | |

**Table 2.** High frequency intramolecular modes in Gly:CA plate.

| Mode | Symbol | α-Gly [22] | assignment |
|------|--------|------------|------------|
| X(ZZ)X | X(YY)X | X(YZ)X |
| 1 | 2971 s | 2973 s | 2973 | v\(_2\)CH\(_2\) |
| 2 | 3008 s | 3007 s | 3009 s | 3008 | v\(_1\)CH\(_2\) |

**Table 3.** Low frequency intermolecular modes in Gly:CA pyramid.

| Mode | Symbol | α-Gly [22] | assignment |
|------|--------|------------|------------|
| Z(YY)Z | Z(XX)Z | Z(XY)Z |
| 1 | 85 vs | 86 vs | 85 vs | 89 | LM |
| 2 | 102 s | 103 s | 102 s | 105 | LM |
| 3 | 149.5 s | 149.5 s | 149.5 s | 141 | LM |
| 4 | 216 m | 216 m | 215 m | 217 | LM |

**Table 4.** High frequency intramolecular modes in Gly:CA pyramid.

| Mode | Symbol | α-Gly [22] | assignment |
|------|--------|------------|------------|
| X(ZZ)X | X(YY)X | X(YZ)X |
| 1 | 2963.7 s | 2963.7 s | 2963.7 m | 2964 | v\(_2\)CH\(_2\) |
| 2 | 2999 s | 3000 s | 3000 | 3000 | v\(_1\)CH\(_2\) |
| 3 | 3100 m | 3099 m | 3107 m | 3098 | vNH(3)…O(1) |
Polarized Raman spectroscopy of Gly:CA single crystals shows that although the addition of croconic acid to the water solution results in yellow color of the grown Gly:CA crystals, this does not significantly change their polymorphic modifications. Gly:CA crystals with pyramidal shape correspond to γ-polymorph, and with plate-like shape to α-polymorph of Gly. The incorporation of CA molecules in the glycine crystal does not change the position of the Raman lines in the high-energy spectrum (2900-3100 \text{ cm}^{-1}), but leads to some shift of the low-energy lines (N3 Table 1 and N3 Table 3), which indicates a possible influence of CA doping on lattice vibrations.

4. Photoluminescence
Luminescence spectroscopy is one of the most widely used techniques in materials science, which yields useful information on electronic structure and the properties of the emitting states in the materials. The photoluminescence of "pure" \( \gamma \)-Gly, along with the weak luminescence band, narrow Raman lines are clearly observed, whose intensity is comparable to that of the luminescence band (inset, fig. 4). Like pure glycine, solid croconic acid is also practically non-luminescent [18]. 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. Thus, almost all luminescence of the doped crystals is a property of the \( \gamma \)-Gly:CA system itself. A similar situation also occurs in the case of \( \alpha \)-Gly:CA.

The room temperature emission spectra of \( \alpha \)- and \( \gamma \)-Gly:CA crystals are shown in figure 4a. The spectra of both \( \gamma \)- and \( \alpha \)-modifications consist of wide structured emission bands with their maxima at 2.50 \text{ eV} (\( \gamma \)-Gly:CA) and 2.56 \text{ eV} (\( \alpha \)-Gly:CA), respectively. Considering that the forbidden gap of \( \gamma \)-glycine crystals is about 5 \text{ eV} [24] the optical electron transitions responsible for the emission involve localized electron states whose energy levels located within the crystal band gap.

![Figure 4](image_url)

**Figure 4.** (a) Emission spectra of \( \gamma \)- and \( \alpha \)-glycine crystals doped with croconic acid. The inset shows the emission spectrum of "pure" \( \gamma \)-glycine. Here R labels the Raman lines. (b) Decomposition of the \( \gamma \)-Gly:CA emission band profile into three Gaussian components. \( \hbar \nu_{exc} = 3.8 \text{ eV} \). \( T = 300 \text{ K} \).

The observed emission-band structure implies the presence of at least three different emitting centers that contribute to the emission of Gly:CA crystals. Figure 4b demonstrates decomposition of the emission band profile (light blue) into three Gaussian components related to the contributions of the three emitting centers in case of \( \gamma \)-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...
croconic acid crystals are practically not luminescent by themselves). The presence of an analogous emission band in the luminescence spectrum of "pure" γ-Gly with a small admixture of citric acid demonstrates that not only croconic acid, but also other organic acids can promote the formation of emitting centers (glycine lattice defects) with the similar structure of radiative transitions.

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