

Laser induced phenomena in γ -glycine crystals

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The photoinduced changes of absorption within the spectral range 200–800 nm and optical second harmonic generation caused by illumination by the cw second harmonic generation of the Nd:YAG laser ($\lambda = 532$ nm) and power about 400 mW were investigated. We have established that increasing the time of illumination by the second harmonic generation of the Nd:YAG laser leads to the occurrence of one strong spectral minimum at 319 nm and another less strong at 420 nm. Increasing the time of illumination leads to a slight red spectral shift of the photoinduced minima. The absence of a substantial increase in temperature indicates that the principal role is played here by the photooccupation of the trapping levels. The effect is observed in a wide spectral range of the incident photoinduced angles, however, the beam should possess a good Gaussian-like form and to be space homogenous. The results were reproduced with precision up to 3–4% which was achieved due to additional stabilization of the photoinduced laser power by double control of the power.

Keywords: optical absorption, organic crystals.

1. Introduction

Recently one can observe a growing interest in the novel class of organic molecular crystals belonging to the triglycine sulfate (TGS) family, including also glycine-salt compounds such as glycine silver nitrate [1] and bis(glycine) manganese chloride dihydrate [2].

Glycine is the simplest amino acid and in compounds it can occur as a cation or an anion or a zwitterion. Unlike other amino acids, it has no asymmetric carbon atom

and is optically inactive. Thanks to its properties it can form many different complexes with inorganic compounds many of which are optically active. Generally, the glycine crystals can be grown in the three different polymorphs: α -, β - and γ -glycine [3]. In Ref. [4], it was established that illumination of the water solution of such crystals may cause transformations from β to γ phases. Moreover, using DSC it was shown that at 189 °C we observe the occurrence of the phase transitions from γ to α phases.

It is crucial that they possess the inherent polarity of the betaine and the zwitterionic glycine molecule which allowed the non-centrosymmetric polar crystals to grow of particular interest were compounds of glycine with inorganic metal halogenides [5, 6]. Particularly interesting appears to be tris(glycine) zinc chloride $(\text{NH}_3\text{CH}_2\text{COO})_3\cdot\text{ZnCl}_2$, which was already described in Refs. [7–11]. Following Ref. [12], the crystal structure consists of isolated clusters connected by hydrogen bonds. Each cluster is composed of one central zinc atom, fourfold coordinated by two chloride ions and two oxygen atoms from two monodentate coordinating glycine molecules, and has the point group symmetry 1. The coordination surrounding of zinc is approximately tetrahedral, but distorted because of the different Zn–O and Zn–Cl distances. In the case of the γ -glycine this structure is additionally modified due to the chemical bond tilting.

In the present work, we will explore the cw laser induced optical properties of the γ -glycine crystals, especially the possibility of exploring their nonlinear optical properties. It is well known that in the organic and semi-organic molecular crystals there exist a natural disordering of the crystalline structure which leads to the formation of a large number of molecular electronic states below the energy gap. Such states form large sub-bands of trapping states participating in the formation of the photo-induced nonlinear optical effects [13, 14]. Such states manifest substantial interactions with the lattice vibrations, *i.e.*, show a good electron–phonon interaction [15]. So, one can expect that the photoinduced effects, in particular nonlinear ones [16], would be crucial for these crystals. The previous studies on the photoinduced optical and non-linear optical effects were done using mainly the pulsed laser treatment [17, 18]. This fact entails principal features of the non-equilibrium processes which substantially complicate such studies. In the present, work we will investigate how the treatment by the continuous laser with the power of about 400 mW for up to 15–20 min would influence the behavior of photoinduced absorption.

2. Experiment – crystal growth

In order to obtain the nuclei of γ -glycine crystals, the AR grade glycine and lithium chloride from Sigma-Aldrich taken at a ratio 1:1 were dissolved in deionised water with a 0.05 μS conductivity at ambient temperature. The foreign impurities were eliminated by multiple recrystallisations. Defect-free crystals were used for seeds. Single crystals of γ -glycine were grown by slow evaporation of the saturated solution at a constant temperature of 305 K. Good quality crystals of the size up to a few cm^3 were obtained after 2 months. Glycine is a biological nutrient and hence microbes grow easily in its aqueous solution. The growth of microbes is detrimental to

the growth of the crystals because they can act as scattering centres in the grown crystal. The solutions were prepared and the crystals were grown in sterile room to eliminate the presence of microbes. The morphology of γ -glycine crystals growing from solution containing lithium chloride reflects the crystal symmetry. The monocrystals have the shape of trigonal pyramids with the $(10\bar{1}1)$ walls best developed. It should be emphasised that the γ -glycine crystals easily break along the planes parallel to the polar axis.

3. Results and discussion

The typical absorptoin of the titled crystlas show that the absorption edge is at about 250 nm (see Fig. 1). However, one can see also some slight maxima at spectral wavelengths 240–560 nm. Such a structure may indicate the occurrence of some additional absorp-tion maxima due to the inter-molecular interaction fragments forming additional molecular sub-bands playing a role of effective trapping levels situated within the forbidden energy gap the forbidden energy gap. Due to the additional laser illumination one can observe re-occupation of these states causing changes in the absorption. At the same time, due to the effective interactions with the phonon lattice states one can expect an occurrence of relatively stable (so-called metastable) states responsible for photoinduced changes.

Molecular organic crystals like and particularly derivatives of triglycine are of an exceptional interest for nonlinear optics and different photoinduced changes. This is a consequence of the large difference between the intra- and intermolecular chemical bonds. Such anisotropy may lead to occurrence of a large number of defect molecular levels within the energy band. For most of the glycine derivatives the electronic energy band gap lies within the 3–5 eV. One can expect that photo irradiation by the laser light with the energies below the energy gap may cause additional photopolarization of the particular trapping levels. As a consequence, this may change to the occupation of the particular trapping states. As a result, excitation by the laser line of different

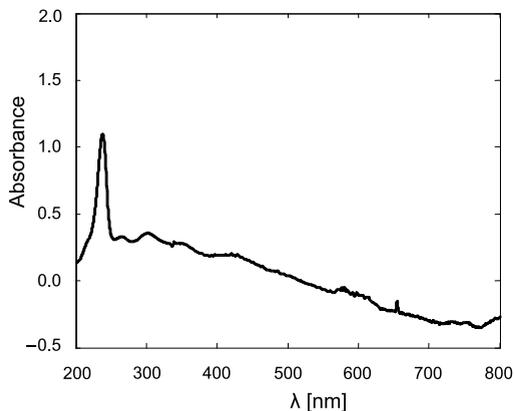


Fig. 1. Absorption spectra of the γ -glycine crystals.

wavelengths may cause changes in their absorption spectra. Moreover, it may substantially change both linear as well as nonlinear optical constants following the simple oscillator models.

In the present work, we have studied the changes of absorption within the spectral range 200–800 nm caused by illumination of the cw second harmonic generation of the Nd:YAG laser ($\lambda = 532$ nm). The measurements were done using an Ocean Optics spectrophotometer with the fiber optics detection. The illumination was done by the 532 nm cw laser. Following the results presented in Figs. 2 and 3, one can clearly see that increasing the time of illumination for the 400 mW Nd:YAG laser leads to occurrence of one strong minimum at 319 nm and another less strong at 420 nm. Increasing the time of illumination leads to some red spectral shift of the photoinduced minima. An absence of substantial increase of temperature indicates that principal role here is played by the photooccupation of the trapping levels. The effect is observed in

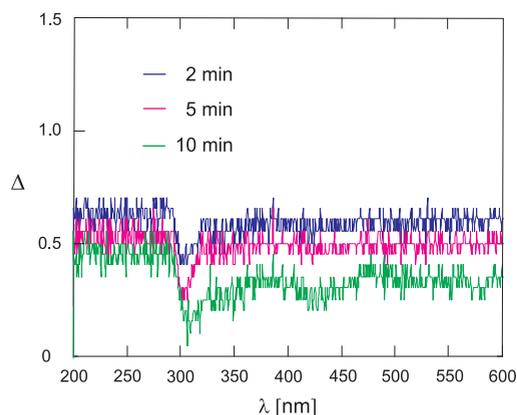


Fig. 2. Photoinduced changes of the γ -glycine samples by the 532 nm cw laser.

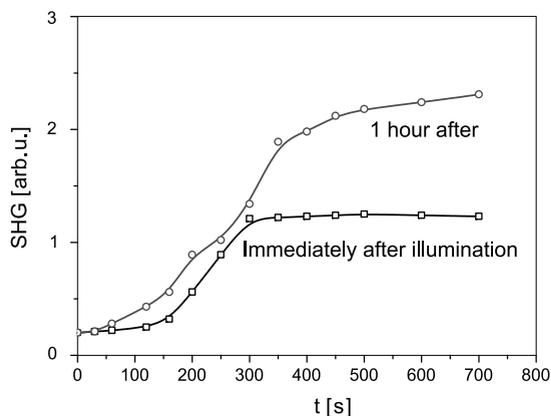


Fig. 3. Dependence of the SHG during illumination at 1064 nm fundamental pulsed laser on the time of treatment.

a wide spectral range of the incident photoinduced angles, however, the beam should possess a good Gaussian-like form and to be space homogenous. The mechanical set-up should give a good heating of the whole photoinduced beam at the same points of the illuminated samples. The results were reproduced with precision up to 3–34%, which was achieved due to additional stabilization of the photoinduced laser power by double control of the power. It is crucial that the effect does not show any anisotropy and the relaxation in time is very slow. Such effect may be promising considering the possibility of laser operation by the optical constants, both linear and nonlinear ones.

At the same time, one can expect that such effect may also change the optical second harmonic generation stimulated by the cw laser beams, which was done by us. For this reason, we have studied the influence of the cw laser beams on the behavior of the SHG. We have used the illumination of crystal powders of the same crystallites to study the output SHG. The Kurtz–Perry method was applied to study the output SHG.

4. Conclusions

We have studied the changes of absorption within the spectral range 200–800 nm caused by illumination of the cw second harmonic generation of the Nd:YAG laser ($\lambda = 532$ nm). The measurements were done using an Ocean Optics spectrophotometer with the fiber optics detection. The illumination was done by the 532 nm wavelength. We have established that increasing the time of illumination for the 400 mW Nd:YAG laser leads to the occurrence of one strong minimum at 319 nm and another less strong at 420 nm. Increasing the time of illumination leads to some red spectral shift of the photoinduced minima. An absence of substantial increase of temperature indicates that principal role here is played by the photooccupation of the trapping levels. The effect is observed in a wide spectral range of the incident photoinduced angles, however, the beam should possess a good Gaussian-like form and to be space homogenous. The results were reproduced with precision up to 3–4%, which was achieved due to additional stabilization of the photoinduced laser power by double control of the power.

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