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$(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal: novel material for detection of γ-radiation by photoinduced nonlinear optical method

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Abstract It was shown a possibility to use the $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal as optoelectronics detectors of gamma-irradiation using photoinduced nonlinear optical methods and photoluminescence. The crystal was irradiated by a ^{60}Co source at ambient conditions. The average energy of the incident γ-rays was about 1.25 MeV. The luminescence excitation was carried out using a 150 mW cw laser with wavelength 532 nm. The best results sensitive to the gamma irradiation were obtained for the third harmonic generations (THG) of the materials treated by bicolor Er: glass laser two beams propagated at angles about 21°–24°. The photoinduced gratings profile also were explored and their correlation with the gamma radiation and nonlinear optical response were explored. Comparison of photoluminescence and photoinduced nonlinear optical sensitivity to radiations was performed.

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1 Introduction

The application of the optical methods for detection of gamma radiation is a promising way for the radiation monitoring [1–3]. These methods are high sensitive and selective, quick and may be used in the different environments.

Compared to the commonly used methods our new attempt: the application of the $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ crystal as the detector material along with photoinduced nonlinear optical method significantly improve the sensitivity to the dose of radiation.

For this reason more important is to use several optical parameters. Normally it is used photoluminescence and one can expect the possible use of photoinduced nonlinear optics [4]. The latter is very sensitive because allows to monitor the higher excited states, take into account contribution of the photopolarized states [5].

Usually, for the radiation, the sensitivity is caused by the presence of the defects states, rare earth dopants, vacancies etc. [6].

New materials and the study of their properties is one of the main directions of modern radiation materials science. The introduction of dopants to binary and ternary compounds [7–10], including rare earth metals [10–12], is a prerequisite for the manufacture of novel optoelectronics radiation detectors. In addition, scientists are paying special attention to the properties of crystalline and amorphous media that are able to consistently show high-intensity photoluminescence and non-linear optical properties under the influence of irradiation [13, 14]. The mechanisms of fluorescent emission and non-linear optical effects are most sensitive to γ-rays due to their high penetrating ability. Therefore the development of radiation-resistant materials and their implementation in space technologies and optoelectronics is one of the main goals of radiation physics and materials science of optoelectronics radiation sensitive materials.

Our previous investigations of the Ga_2S_3–In_2S_3 system [15] found two ternary compounds, $GaInS_3$ and $Ga_{0.7}In_{1.3}S_3$. $GaInS_3$ forms in a peritectic reaction $L + In_2S_3 \leftrightarrow GaInS_3$ at 1190 K, crystallizes in the hexagonal symmetry, SG $P6_1$, $a = 0.6655(4)$ nm, $c = 1.7950(3)$ nm, and has a homogeneity region that stretches within 47–57 mol% In_2S_3 at 820 K. An Erbium-doped single crystal of the $GaInS_3$ phase, $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$, was grown using the technique described in detail in [15].

We used X-ray photoelectron spectroscopy (XPS) to investigate core-level and valence-band spectra of pristine and Ar^+ ion-bombarded surfaces of the $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal [16]. It was determined that the single crystal is very resistant to Ar^+ ion-bombardment. For instance, such treatment did not cause any substantial changes of the binding energies of the core-level electrons, or of the shape of XPS core-level and valence-band spectra. It was suggested in [16] that the addition of Erbium into the $(Ga_{55}In_{45})_2S_{300}$ lattice does not lead to significant changes in the particularities of the chemical bonding of the original (undoped) single crystal.

The objective of this work is to study the possibility to apply photoinduced third harmonic generation and to compare it with the photoluminescence spectra of non-irradiated and irradiated with different doses of γ-rays single crystal of $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$. Finally, we compared two methods, first based on the investigations of luminescence intensity versus radiation dose and second THG versus radiation dose. We have shown that while both optical methods allow for the determination of dose, THG is definitely more sensitive.

2 Experimental

The $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal was grown by the solution-melt method that is described in detail in [15]. The diffraction pattern of the specimen that was cut from the middle part of the single crystal (scan step 0.05°, exposure time 27 s) have shown that the sample possesses single-phase and they were identified in space group $P6_1$, $a = 0.6657(3)$ nm, $c = 1.7962(4)$ nm [15].

The photoluminescence spectra were investigated using an MDR-206 monochromator at room temperature with spectral resolution 1 nm. The signal was registered by Si and a PbS-based photodetector. The luminescence excitation was performed by a diode pumped second harmonic generated Nd:YAG laser was performed by a cw 150 mW laser (model LDM532U) at the wavelength 532 nm. The crystal was irradiated by a ^{60}Co source at ambient conditions (Fig. 1). The average energy of the incident γ-rays

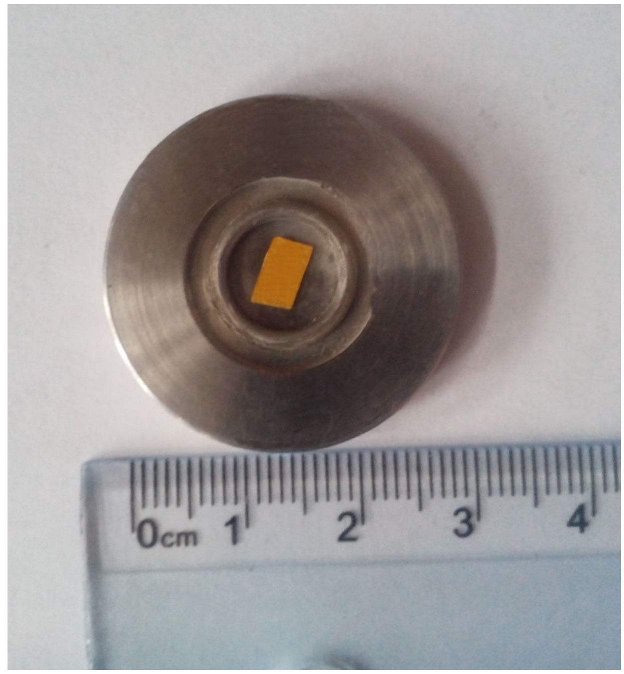

Fig. 1 Irradiation of the $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal by a ^{60}Co source

was equal to about 1.25 MeV. Absorbed dose was controlled using a VDEG2-34 SP-1 device for the detection and measurement of γ-rays. The energy range of the γ-radiation detection was varied within the 0.05–3 MeV. The single crystal was irradiated by doses 420, 1260, 2520, and 5040 Gy.

Additionally, we measured the radial distribution of γ-quanta of the source (dependence of the number of γ-quanta on the distance from the source center) in two mutually perpendicular directions. The exposure time for the γ-quanta detection was 300 s. Each measurement was repeated fivefold, and the number of γ-quanta was averaged. The measurement results are presented in Table 1.

The highest intensity of γ-quanta emission is found in the source center and it was decreased gradually upon distancing. This fact may cause the non-uniform distribution of the radiation-induced defects in the crystal which particularly affects its non-linear optical properties.

3 Results and discussion

3.1 Photoluminescence

We investigated the visible and NIR emission spectra (Fig. 2a, b) of the original single crystal of $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ and the specimen irradiated with

Table 1 Radial distribution of γ-quanta for the ^{60}Co radioactive source

	Distance from the center (mm)				
Direction	−4	−2	0	+2	+4
X	6315	6523	6768	6627	6555
Y	6200	6468		6589	6393

different doses of γ-rays at ambient temperature under laser excitation with 532 nm wavelength.

Strong emission bands are observed in the visible and near-IR regions, with maxima at 810 and 1540 nm which correspond to the radiation transitions of Erbium ions, $^4I_{9/2}\rightarrow{}^4I_{15/2}$, $^4I_{13/2}\rightarrow{}^4I_{15/2}$ respectively. The location and the shape of the emission spectra in all samples are the same, the intensities of both peaks increase at radiation dose 2500 Gy. With increasing the dose of irradiation till 5060 Gy, the intensity of the peak at 810 nm is almost unchanged (comparatively with the intensity of the photoluminescence of the single crystal specimen irradiated by dose 2500 Gy) (Fig. 2a), and the intensity of the maximum at 1540 nm slightly decreases (Fig. 2b).

The diagram of energy levels of the Er^{3+} ions (Fig. 3) was employed to understand the emission mechanism. The excitation with 532 nm wavelength boosts erbium ions from the ground state to $^2H_{11/2}$.

Erbium ions cannot undergo non-radiative relaxation to $^4I_{9/2}$ state which is responsible for the 810 nm emission due to high energy distance between the states $^4S_{3/2}$–$^4F_{9/2}$ and $^4F_{9/2}$–$^4I_{9/2}$. Therefore, the excitation of states $^4I_{9/2}$ is resulted from the cross-relaxation process.

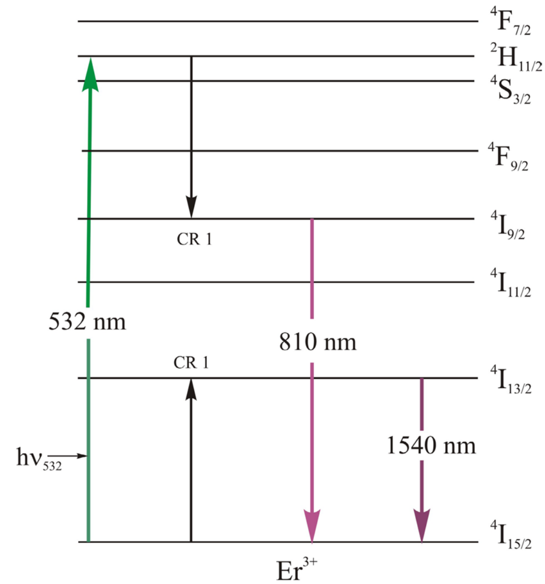

Fig. 3 Diagram of energy levels in erbium ions

The cross-relaxation involves adjacent erbium ions in the states $^2H_{11/2}$ and $^4I_{15/2}$, after which the former ion transits to $^4I_{9/2}$ state, and the other to $^4I_{13/2}$ state according to the formula:

$$^2H_{11/2}+{}^4I_{15/2}\rightarrow{}^4I_{9/2}+{}^4I_{13/2} \quad (1)$$

The diagram (Fig. 3) shows that such mechanism results in large numbers of erbium ions in excited states $^4I_{9/2}$, $^4I_{13/2}$ which are involved in the luminescent emission. Additionally, we suggest that high radiation doses (2500, 5060 Gr)

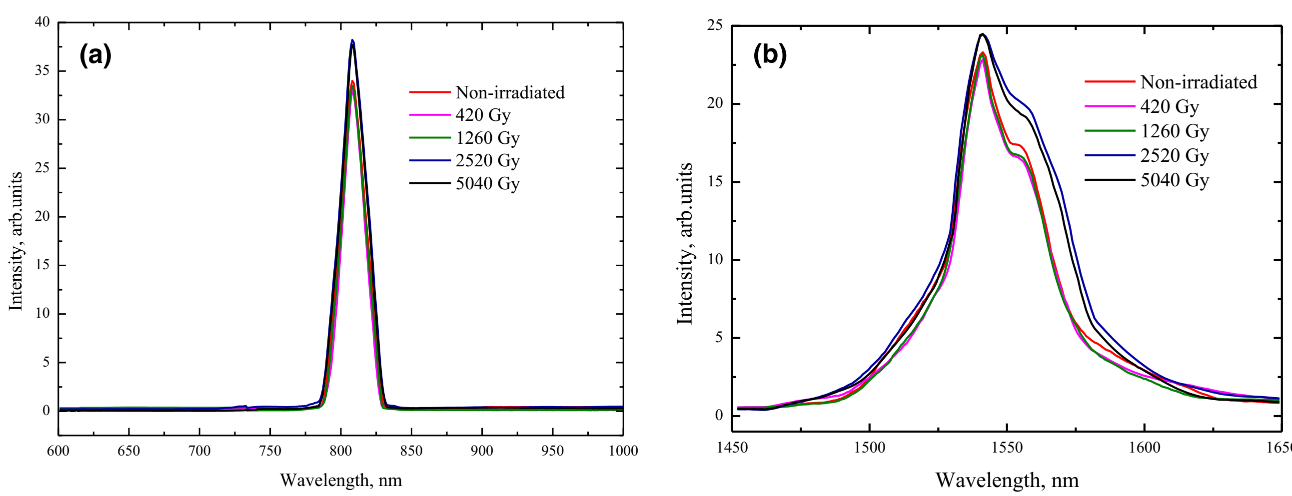

Fig. 2 Visible and NIR emission spectra of original and γ-irradiated $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal in **a** 600–1000 nm, and **b** 1450–1650 nm wavelength regions

generate a substantial concentration of phonons with energy and momentum that are necessary for the cross-relaxation of adjacent erbium ions. Therefore luminescence intensity would increase at higher radiation doses, as observed in Fig. 2.

Unlike the single crystal that was investigated in this work, the glassy sulfide alloys [11, 12] exhibit many emission bands but with lower intensity. This is because erbium ions in glasses may occupy several positions, and each may provide photoluminescent radiation. Also, γ-irradiation of the glasses [17] changes the mechanism of the luminescence emission. Whereas, no significant changes in the luminescence spectra were found after γ-irradiation of the $(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal, which determines its advantage in radiation resistance for the possible applications in optoelectronics.

3.2 Non-linear optical properties (third harmonic generation)

Contrary to the materials, which use only the photoluminescence in the present work we will try to propose some multi-functional materials. For instance, a material, which possesses additionally the high photoinduced nonlinear optical sensitivity. That means—it may be used at least two independent methods. The first tone was more traditional PL described above and the second one was connected with the photoinduced nonlinear optics using a photoinducing beams of the coherent beams with two coherent wavelengths at 1540 and 770 nm. The beams correspond to the fundamental and doubled frequency (due to second harmonic generation) of Er: glass 20 ns laser beam diameter about 3 mm and of the Gaussian like form with

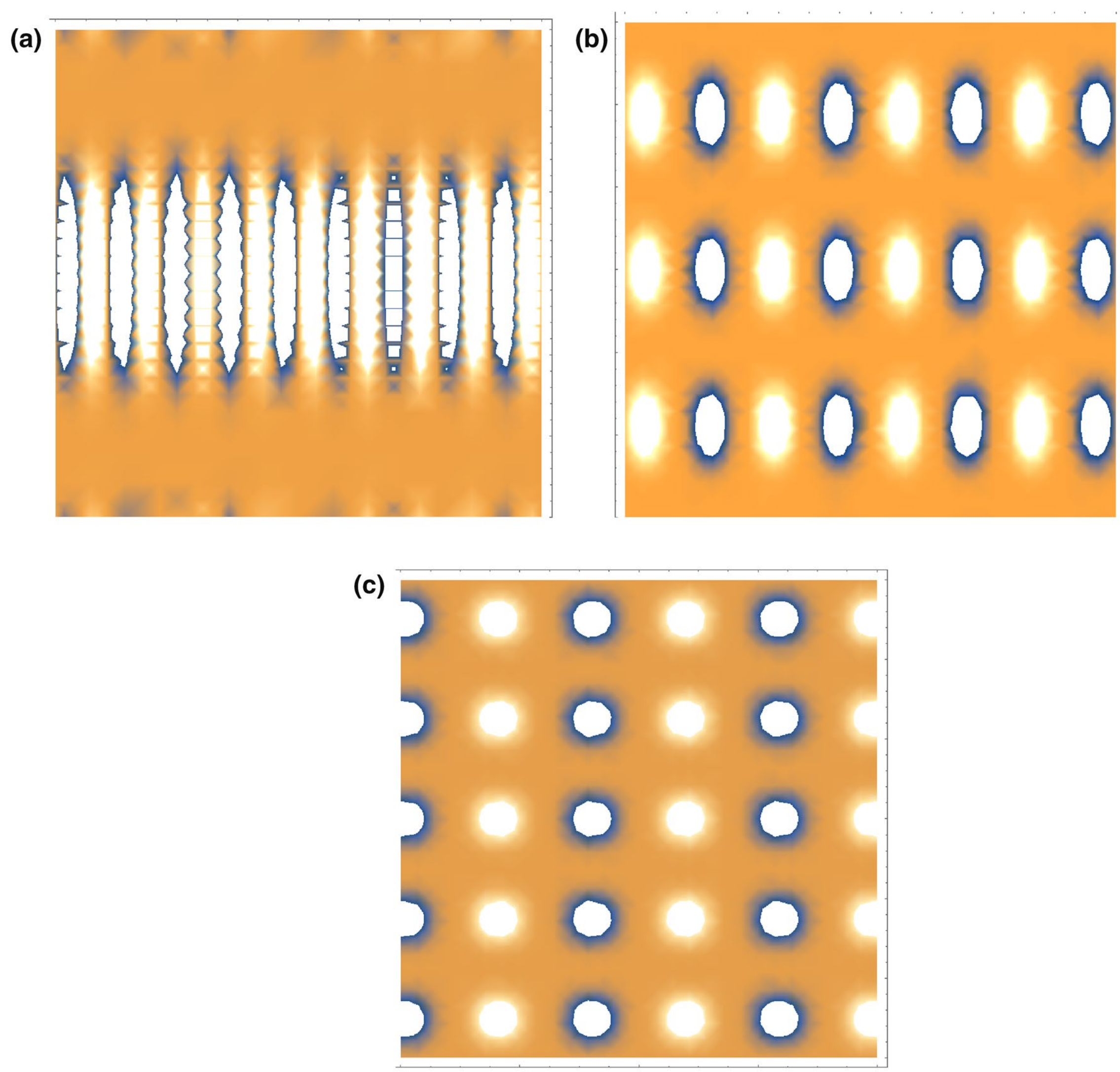

Fig. 4 Computationally reconstructed changes of the bicolor induced gratings at the same conditions for the 1540/770 nm bicolor coherent laser treatment for different doses: **a** 1250 Gy; **b** 2520 Gy; and **c** 5040 Gy. The detection was performed using the cw He–Ne laser beam at 1150 nm

frequency repletion 10 Hz and wavelength 1540 nm using a scheme similar to the described in the Ref. [18]. We have found that for the titled crystal the optimal angle was varied within the degree and the process of the duration treatment up to 2–3 min and additionally the dc-electric field with frequency 50 Hz and voltage about 2 kV was applied.

As a consequence after the treatment there occurred the space grating. For the different radiation doses, they are shown in the Figs. 4 and 5. One can see that depending on the gamma radiation doses the general view of this picture were substantially different. First of all the space distribution of the diffracted beams were quite different. The shapes of the optical quasi-interferometer reflexes as well as their space frequencies also were quite different and the studied third harmonic generation for fundamental wavelengths 1540 nm have shown some correlation with the dose dependence the third harmonic maxima. So the laser induced bicolor coherent gratings may be very crucial here. And as for the case of photoluminescence (Fig. 2) the maximal value are obtained for the dose 2520 Gy. So one can say about the existence of some maxima in optoelectronic parameters versus the gamma radiation doses.

The such differ cases are also caused by a fact that for the nonlinear optical responses the contributions are presented both from active nonlinear optical polyhedral and surrounding long range ordered background [19, 20]. As a consequence [21], these contributions should be more sensitive.

4 Conclusions

The novel type of the optoelectronics materials for sensing of gamma-radiation is proposed based on

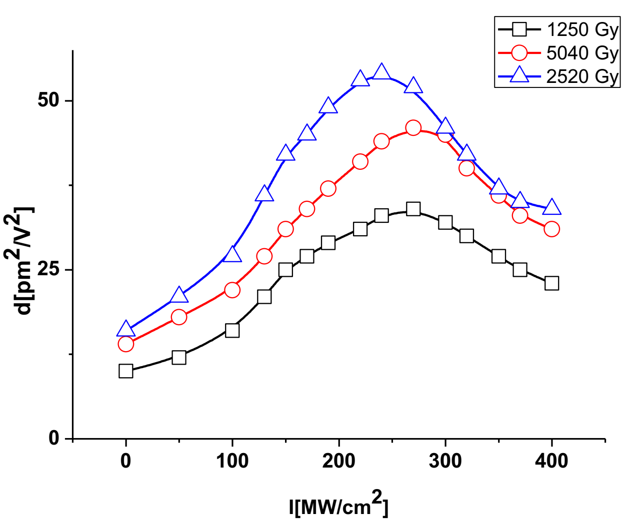

Fig. 5 Dependent of the third order optical susceptibilities versus the power density of the bicolor Er: glass laser excitations

$(Ga_{54.59}In_{44.66}Er_{0.75})_2S_{300}$ single crystal. The strong emission bands detected at 810 and 1540 nm correspond to the radiation transitions $^4I_{9/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of Erbium ions, respectively. At the same time use of the two bicolor treatment by Er: glass laser at 1540/770 nm of the THG have shown that the photoinduced nonlinear optical method gives higher sensitivity. The obtained data allow proposing the bicolor treated methods for detection of the gamma radiation as more efficient tools for radiation detection with respect to the traditional photoluminescent methods.

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