Color Centers in $Ca_4GdO(BO_3)_3$ Single Crystals Irradiated by Gamma Quanta

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The present work is devoted to investigation of optical absorption in pure $Ca_4GdO(BO_3)_3$ single crystals in the spectral range 0.2–1.1 μm induced under influence of the gamma quanta irradiation with absorbed dose 2×10^3 Gy. The effect of heating in air on the absorption spectrum of irradiated sample is also studied.

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1. Introduction

A great interest in non-linear optical materials used for frequency conversion and for self-frequency doubling lasers has been observed in the last years. Recently, Nd-doped $YAl_3(BO_3)_4$, $LiNbO_3$, $Li_2B_4O_7$ and LiB_3O_5 have been reported as very efficient non-linear optical crystals for achieving self-frequency doubling in the green part of the spectrum [1–3].

Undoped single crystals of gadolinium calcium oxoborate ($Ca_4GdO(BO_3)_3$; GdCOB) are piezoelectronics elements and optical planar waveguides [4], while crystals doped with rare-earth ions (Nd, Yb, Eu, Er, Tm) are new and promising laser materials. By combining the non-linear properties of the GdCOB matrix and the laser emission due to Nd^{3+} ions, it is possible to high-efficient generate directly by self-frequency doubling of green (at 530.5 nm) and blue (at 468 nm) laser light [5]. The main advantage of GdCOB, comparing with other borates is large transparent range (320–2700 nm), high damage threshold (above 1 GW/cm^2 at 530 nm) and non-hygroscopic [6]. The material melts congruently at near 1750 K and its viscosity is not very high, so the Czochralski technique was successfully used to easy obtain pure and heavy neodymium or ytterbium doped GdCOB single crystals [7–9].

It is very well known that the color centers are induced in laser crystals under the influence of ionizing and UV radiation [10]. Usually, the color centers are detrimental for laser generation efficiency. For example, in neodymium doped gadolinium gallium garnet crystals the color centers absorb pump light radiation diminishing pumping efficiency and re-absorb the laser radiation [11].

Some works are devoted to complex investigation of color centers in non-linear optical oxide crystals as $LiNbO_3$, $Li_2B_4O_7$, etc., for example [10]. The $Li_2B_4O_7$ crystals possess an interesting property, namely the color centers practically do not appear due to ionizing radiation influence [10]. On the other hand, the $LiNbO_3$ crystals are very sensitive for color centers creation [10]. In this way, the study of influence of ionizing radiation on optical properties of GdCOB crystals and color centers creation in these crystals are necessary.

In this work the results of investigation of the influence of gamma quanta on optical properties of GdCOB are presented and the origins of color centers are discussed. The purpose of this work is to determine the nature of color centers produced in the GdCOB crystal after irradiation by gamma quanta.

2. Experiment

The GdCOB single crystals of about 25 mm in diameter and 50 mm long was grown in the Institute of Electronic Materials Technology (Warsaw) by the Czochralski technique from iridum crucible. Growth was carried out in nitrogen atmosphere. The seeds were oriented along the [010] direction. The crystals were colourless and perfectly transparent, without any visible macroscopic defects. More detailed information about crystal growth is presented in [7].

The sample for the investigation of crystal optical properties before and after gamma quanta irradiation was made in the form of plane-parallel polished plate of 1.2 mm thickness.

The sample was irradiated with gamma quanta from ^{137}Cs source with average energy of 0.661 MeV and absorbed dose 2×10^3 Gy in the Tadeusz Kościuszko Land Forces Military Academy in Wrocław.

After gamma quanta irradiation, the isochronous heating in air (by time 15 min in each of the cycle) was performed by using a LHT 04/16 NABERTHERM furnace with C42 controller. The temperature during each heating was stable with measuring accuracy ±1 K, but different for each of the cycles (ranging from 320 K to 530 K).

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The crystal absorption was studied using a UNICAM UV 300 spectrophotometer. The additional absorption (AA) value ΔK induced by external influence was determined as

$$\Delta K = \frac{1}{d}\ln\frac{T_1}{T_2}, \qquad (1)$$

where d is the sample thickness, T_1 and T_2 are the sample transmission coefficients before ("as grown") and after treatment (i.e. gamma irradiation or each step of heating), respectively. The heating sample transmission spectrum was measured after it was cooled to the room temperature.

3. Results and discussions

The absorption spectrum of as grown GdCOB crystal (before gamma quanta irradiation) measured in the wavelength region between 50000 cm^{-1} and 9000 cm^{-1} is shown in Fig. 1.

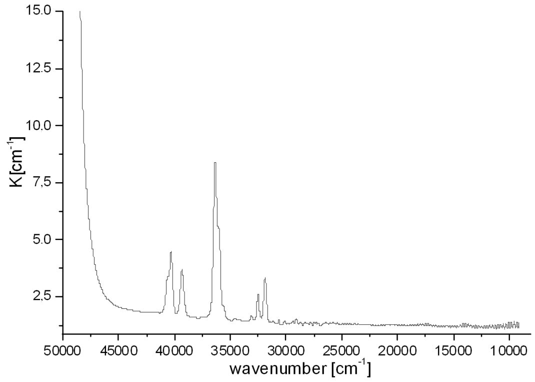

Fig. 1. The absorption spectrum of as grown GdCOB crystal.

The fundamental absorption edge of crystal is above 47000 cm^{-1}, in the region below the crystal is transparent. The absorption spectrum of the GdCOB sample exhibits a small absorption coefficient value in the wave number region between 31250 cm^{-1} and 9000 cm^{-1} and broad absorption bands of color centers are not present. There is a convincing evidence for a good optical quality of this crystal.

In the UV region the three groups of intensive absorption peaks near 40160 cm^{-1}, 36360 cm^{-1} and 32260 cm^{-1} are observed. These groups corresponding with Gd^{3+} transitions from $^8S_{7/2}$ ground state to the ^6D_J, ^6I_J, and ^6P_J excited levels, respectively [6, 7].

After irradiation by gamma quanta with dose 2×10^3 Gy the growth of absorption in crystal transparence region is observed and wide AA in the region 47000–16000 cm^{-1} with maxima near 21800 cm^{-1}, 28000 cm^{-1}, 38500 cm^{-1}, 43000 cm^{-1} arise in GdCOB crystal spectrum (Fig. 2). Also a clearing near the edge of fundamental absorption (optical bleaching) above 47000 cm^{-1} take place (Fig. 2).

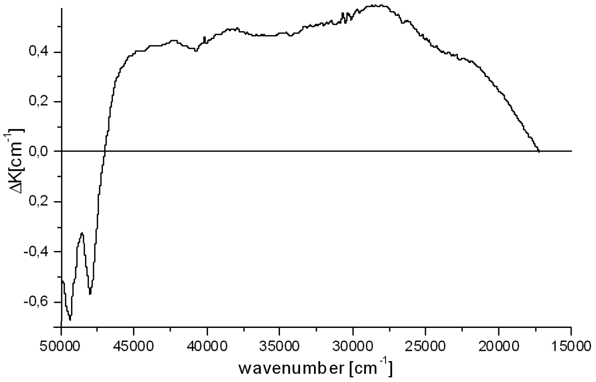

Fig. 2. AA of gamma quanta irradiated GdCOB crystal.

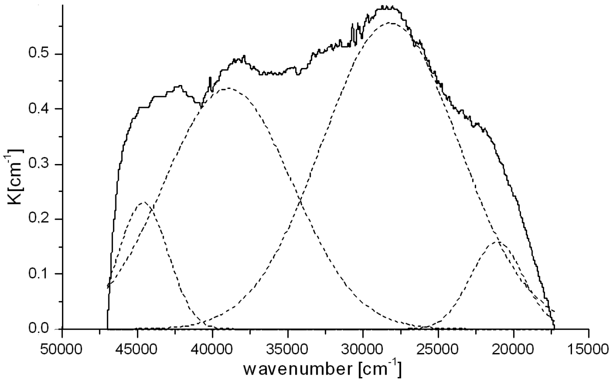

Fig. 3. The fitting of AA of GdCOB spectrum into Gaussian bands.

The fitting of AA spectrum into Gaussian bands give 4 single bands with maximum at 44614 cm^{-1}, 38987 cm^{-1}, 28203 cm^{-1} and 21115 cm^{-1} (Fig. 3). The additional fitting parameters (amplitude and half-width) are given in Table I.

The color centers connected with AA have poor thermal stability. The AA of gamma quanta irradiated GdCOB crystal can be partially removed by annealing in air in temperature 373–453 K in the time 15 min (Fig. 4). It is clear that for the initial stage of heating the color centers disappear with different dynamics. In the first annealing step (at temperature 373 K) most intense disappearing of 28203 cm^{-1} band was observed (Fig. 4),

TABLE I

The fitting parameters of AA of GdCOB spectrum into Gaussian bands.

Gauss component	Band max	Amplitude	Half-width
	[cm^{-1}]		
G1	44614	0.231	3261
G2	38987	0.437	4683
G3	28203	0.556	9109
G4	21115	0.157	3470

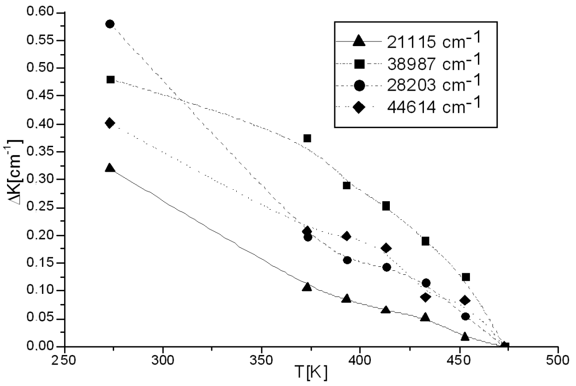

Fig. 4. Thermal decay of additional absorption of GdCOB crystal.

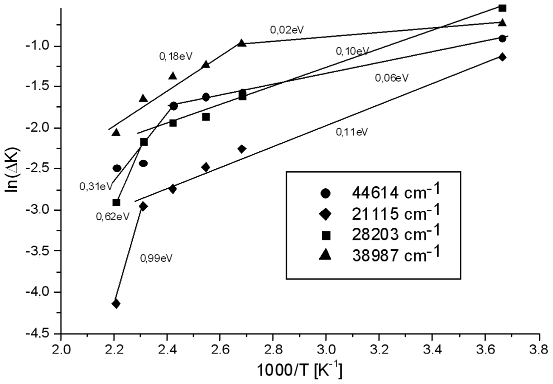

Fig. 5. Thermal decay kinetics of AA in Arrhenius coordinates.

while for the other bands the dynamics of disappearance are similar and smaller. On the other hand, for higher annealing temperature (413–473 K) the band 28203 cm^{-1} disappears near similar than other bands. The last step annealing in temperature 473 K leads to the complete AA disappearing. The poor thermal stability is typically for color centers created in oxide crystals due to the trapping of charge carrier by native defects (for example F-type centers, O^- centers stabilized by lattice distortion) or charge change of uncontrolled impurities (Fe, Cr, Mn ions, etc.) [10]. We note that the optical bleaching of crystal near the fundamental absorption edge was early observed in garnets as a result of charge change of uncontrolled impurities (I_{m}) due to electron trapping (according rule $I_{\mathrm{m}}^{n+} + \mathrm{e}^- \rightarrow I_{\mathrm{m}}^{(n-1)+}$) [10, 12].

TABLE II

The activation energy for thermal decay of AA in GdCOB crystal.

Band [cm^{-1}]	Activation energy [eV]	
21155	0.11 (below 433 K)	0.99 (above 433 K)
28203	0.10 (below 433 K)	0.62 (above 433 K)
38987	0.02 (below 373 K)	0.18 (above 373 K)
44614	0.06 (below 393 K)	0.31 (above 393 K)

The isochronous heating of the irradiated sample shows that the thermal decay of AA is connected with absorption growth above 47000 cm^{-1}.

The experimental data analysis in the Arrhenius coordinates (on the y-axis there is indicated the natural logarithm of AA and on the axis x — $1000/T$, where T is the temperature of annealing) show that the absorption coefficient dependence on annealing temperature can be well approximated by two straight lines (Fig. 5). The estimated activation energies are given in Table II. All defects connected with AA have been annealed in two-stage processes, but with different activation energy (Table II).

4. Conclusions

Irradiation the GdCOB crystal by gamma quanta leads to the creation of color centers connected with genetic defects and impurities. These centers are removed completely after annealing at temperature 473 K. All of this centers decay with two-stage processes.

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