Color centers in $Ca_4GdO(BO_3)_3$ single crystals irradiated by gamma quanta

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Abstract

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 $2x10^3$ 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 1750K 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.

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 $2x10^3$ Gy in The Tadeusz Kosciuszko Land Forces Military Academy in Wroclaw.

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 ±1K, but different for each of the cycles (ranging from 320K to 530K).

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 50 000 cm^{-1} and 9 000 cm^{-1} is shown in Fig 1.

The fundamental absorption edge of crystal is above 47 000 cm^{-1}, in the region below the crystal is transparent. The absorption spectrum of the GdCOB sample exhibit a small absorption coefficient value in the wavenumber region between 31 250 cm^{-1} and 9 000 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 40 160 cm^{-1}, 36 360 cm^{-1} and 32 260 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 21 800 cm^{-1}, 28 000 cm^{-1}, 38 500 cm^{-1}, 43 000 cm^{-1} arise in GdCOB crystal spectrum (Fig2). Also a clearing near the edge of fundamental absorption (optical bleaching) above 47000 cm^{-1} take place (Fig2).

The fitting of AA spectrum into Gaussian bands give 4 single bands with maximum at 44 614 cm^{-1}, 38 987 cm^{-1}, 28 203 cm^{-1} and 21 115 cm^{-1} (Fig.3). The additional fitting parameters (amplitude and half-width) are given in Table 1.

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 373K – 453 K in the time 15 min. The last step annealing in temperature 473 K lead 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 (Im) due to electron trapping (according rule $Im^{n+} + e^- \rightarrow Im^{(n-1)+}$) [10,12].

The isochronous heating of the irradiated sample shows that the thermal decay of AA is connected with absorption growth above 47 000 cm^{-1}.

The experimental data analysis in Arrhenius coordinates (Fig 4) show that the absorption coefficient dependence on annealing temperature can be well approximated by two straight lines. The estimated activation energies are given in Table 2. The all defects connected with AA have been annealed in two-stage processes, but with different activation energy (Tab 2).

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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Table captions

Table 1 . The fitting parameters of AA of GdCOB spectrum into Gaussian bands

Table 2. The activation energy for thermal decay of AA in GdCOB crystal

Figure captions

Fig1. The absorption spectrum of as grown GdCOB crystal

Fig 2. AA of gamma quanta irradiated GdCOB crystal

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

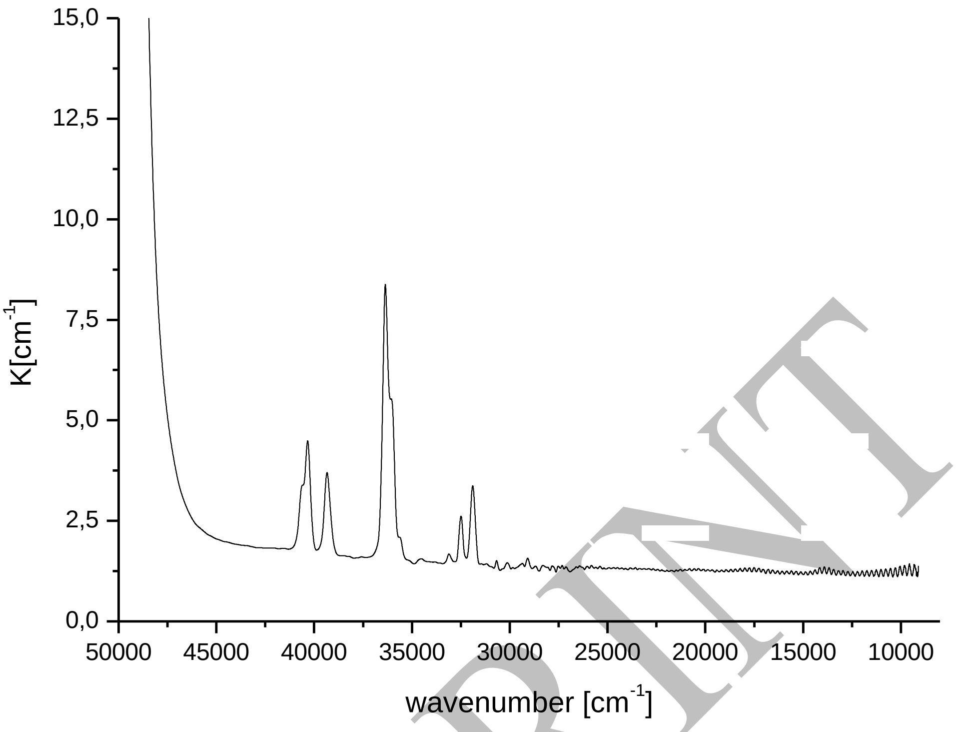
Fig 4. Thermal decay kinetics of AA in Arrhenius coordinates

Table 1

Gauss component	band max	amplitude	half-width
G1	44614 [cm^{-1}]	0,231 [cm^{-1}]	3261 [cm^{-1}]
G2	38987 [cm^{-1}]	0,437 [cm^{-1}]	4683 [cm^{-1}]
G3	28203 [cm^{-1}]	0,556 [cm^{-1}]	9109 [cm^{-1}]
G4	21115 [cm^{-1}]	0,157 [cm^{-1}]	3470 [cm^{-1}]

Table 2

Band	Activation energy	
21155 [cm^{-1}]	0,11 [eV] (below 433[K])	0,99 [eV] (above 433[K])
28203 [cm^{-1}]	0,10 [eV] (below 433[K])	0,62 [eV] (above 433[K])
38987 [cm^{-1}]	0,02 [eV] (below 373 [K])	0,18 [eV] (above 373 [K])
44614 [cm^{-1}]	0,06 [eV] (below 393 [K])	0,31 [eV] (above 393 [K])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7,5
5,0
2,5
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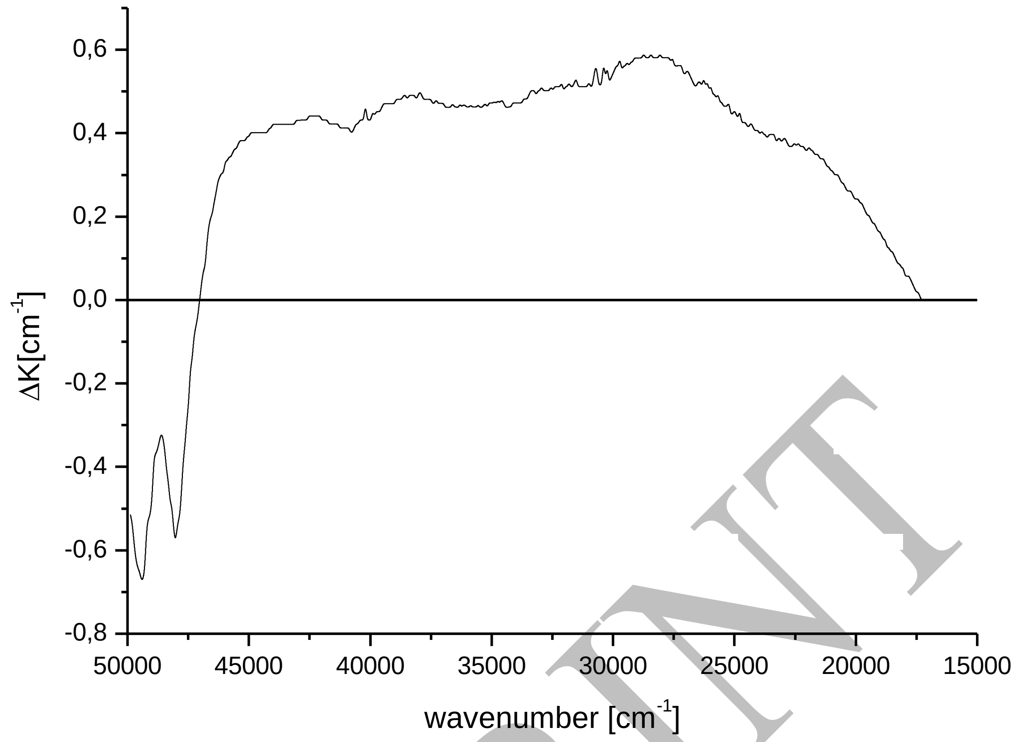
45000
40000
35000
30000
25000
20000
15000
10000
wavenumber [cm-1]

Fig 1



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0,2
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-0,4
-0,6
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40000
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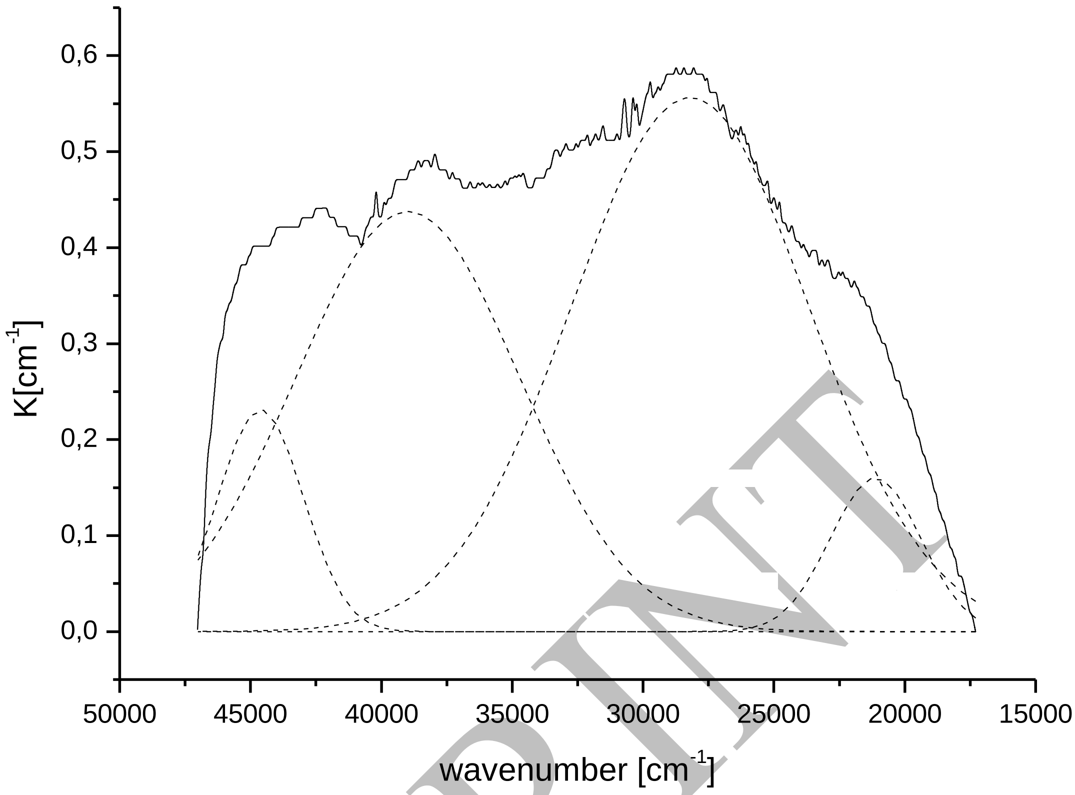
30000
25000
20000
15000
wavenumber [cm-1]

Fig 2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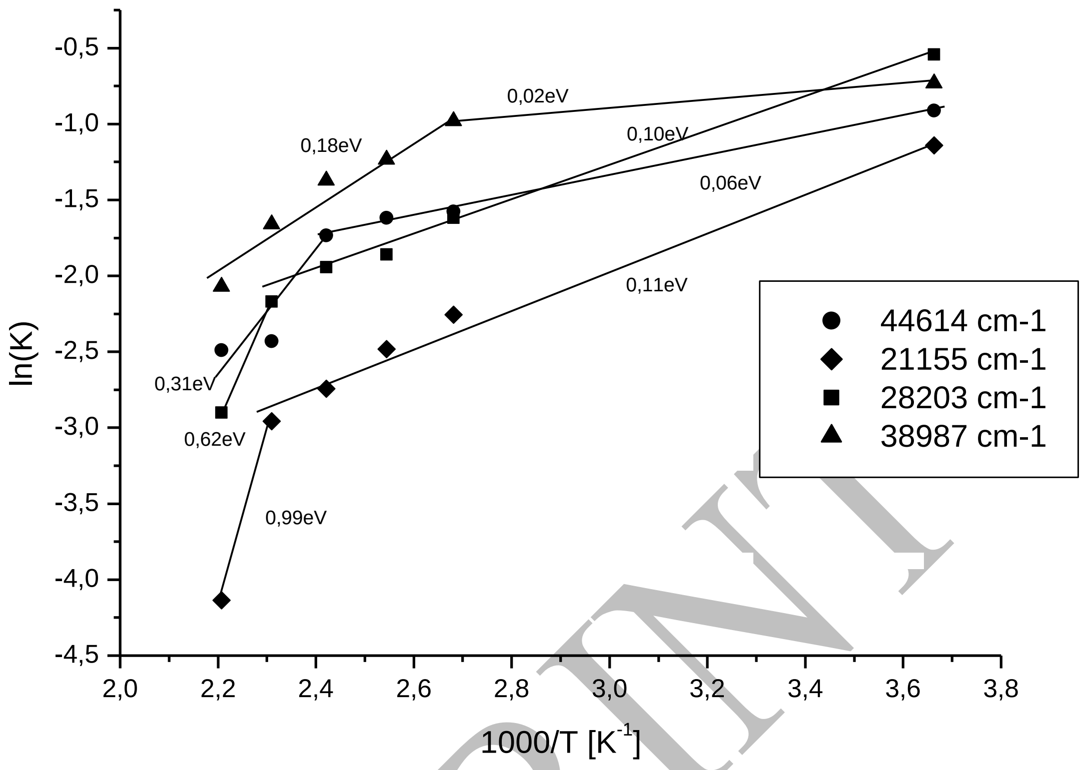
wavenumber [cm-1]

Fig 3



ln(K)
1000/T [K-1]
44614 cm-1
21155 cm-1
28203 cm-1
38987 cm-1
0,02eV
0,18eV
0,10eV
0,06eV
0,11eV
0,31eV
0,62eV
0,99eV

Fig 4