Influence of the proton irradiation on the optical properties of garnet $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0,1,2,3) single crystals

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Presented at Virtual Session of RAD2022

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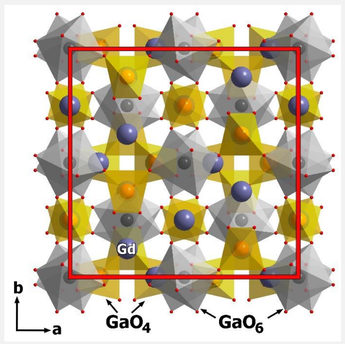
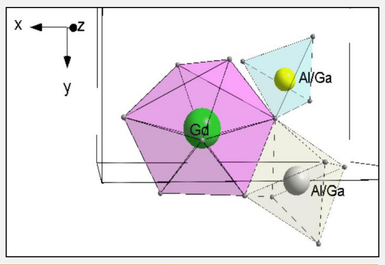
Motivation

The Ce-doped garnet scintillating crystals with general formula $Gd_3(Al,Ga)_5O_{12}$ (GAGG) are perspective for medical applications, e.g., in a single photon emission computed tomography and in high-energy physics. These crystals attract attention due to the combination of high density, chemical stability, very high light yield and reasonable energy resolution. Radiation resistance is an essential parameter for scintillators. Previously it was shown that GAGG crystals demonstrate induced absorption under irradiation with electrons and protons [10.1134/S1027451021060318; 10.1016/j.nima.2018.11.101]. However, these previous studies were mainly focused on GAGG compositions with x = 2,3, which are considered as most perspective for application as scintillators. Here we present the study of the interrelation between the composition of $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0,1,2,3) mixed crystals and intensity of induced absorption bands after proton beam irradiation.

Garnet crystal structure



- GAGG has cubic structure with a space group of *Ia3d*;
- The general chemical formula $A_3B_2^{oct}C_3^{tet}O_{12}$ contains three types of oxygen polyhedrons;
- Gd^{3+} occupies dodecahedral sites while Al^{3+} and Ga^{3+} are distributed between octahedral and tetrahedral sites.



	A – site dodecahedral	B - site octahedral	C - site tetrahedral
$Gd_3(Al,Ga)_5O_{12}$	Gd^{3+} (0.105 nm)	Ga^{3+} (0.062 nm) Al^{3+} (0.054 nm)	Ga^{3+} (0.047 nm) Al^{3+} (0.039 nm)

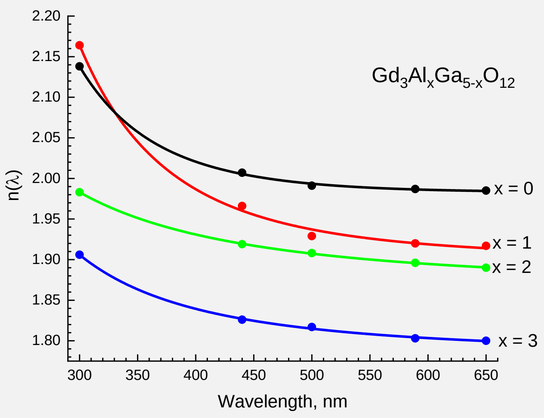
Undoped $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0, 1, 2 and 3) single crystals were grown by the Czochralski method at the Fomos-Materials (Moscow, Russia, https://newpiezo.com/).

Mixed garnet's composition and site occupancy

Nominal composition	$Gd_3Al_1Ga_4O_{12}$	$Gd_3Al_2Ga_3O_{12}$	$Gd_3Al_3Ga_2O_{12}$
Composition after the Rietveld refinement	$Gd_3Al_{1.93}Ga_{3.07}O_{12}$	$Gd_3Al_{2.68}Ga_{2.32}O_{12}$	$Gd_3Al_{3.52}Ga_{1.48}O_{12}$
Ga:Al ratio after the Rietveld refinement	1.59	0.87	0.42
Occupancy B	0.539(4)Ga^{3+} 0.461(4)Al^{3+}	0.336(4)Ga^{3+} 0.664(4)Al^{3+}	0.221(4)Ga^{3+} 0.779(4)Al^{3+}
Ga:Al ratio in B	1.17	0.51	0.28
Occupancy C	0.661(4)Ga^{3+} 0.339(4)Al^{3+}	0.549(4)Ga^{3+} 0.451(4)Al^{3+}	0.346(3)Ga^{3+} 0.654(3)Al^{3+}
Ga:Al ratio in C	1.95	1.22	0.53
Calculated density, g/cm³	6.60	6.47	6.28

Table. Selected crystallographic data for $Gd_3Al_xGa_{5-x}O_{12}$ (x = 1, 2 and 3) samples from [D. Spassky et al, Opt. Mater. 125 (2022) 112079].

Refraction coefficients of $Gd_3Al_xGa_{5-x}O_{12}$



Spectral dependence of refraction coefficient n(λ) for $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0,1,2,3) single crystals obtained using Brewster's law method (dots) and its approximation using Cauchy equation (line).

- **Refraction coefficients were determined using the multiangle spectrophotometry method based on the Brewster's law:**

$$tg\ \varphi_{Br} = n/n_0,\ \text{where}$$

n – refraction coefficient of the sample,
n0 – refraction coefficient of the air (n0 = 1),
φ_{Br} – Brewster angle.

- **The general tendency of the refraction index decrease with increase of Al content is observed.**
- **The spectral dependences of refraction coefficient were further approximated using Cauchy equation:**

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

where A, B and C – characteristic constants.

- **The approximation has been performed using the constants presented in Table.**

Nominal composition				
Parameters	$Gd_3Ga_5O_{12}$	$Gd_3Al_1Ga_4O_{12}$	$Gd_3Al_2Ga_3O_{12}$	$Gd_3Al_3Ga_2O_{12}$
A	1.99	1.90	1.87	1.78
B	5381	1150	10167	6862
C	$1.70\cdot10^9$	$2.04\cdot10^9$	$3.1\cdot10^7$	$3.97\cdot10^8$

Acknowledgements

The research was supported by Russian Foundation for Basic Research №20-02-00688.

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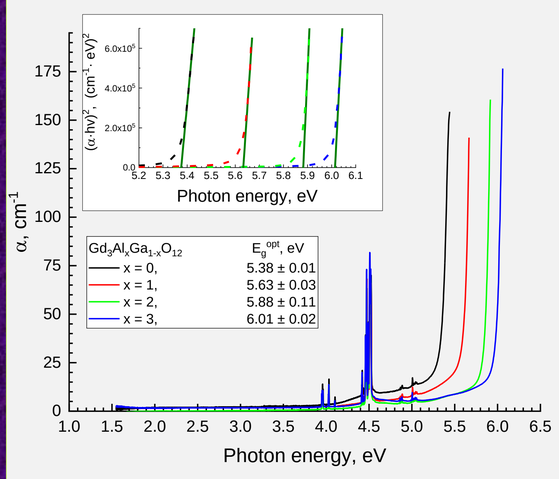
Experimental techniques

Absorption spectra were measured using PerkinElmer Lambda 950 spectrophotometer with spectral resolution 0.2 nm. Reflection spectra were measured using Cary-5000 spectrophotometer with universal measurement accessory.

Irradiation by protons with energy 6.7 MeV was performed using 120 cm cyclotron at Skobeltsyn Institute of Nuclear Physics. The path length of protons with this energy in the studied crystals is about 140 μm.

Absorption spectra of $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0,1,2,3)

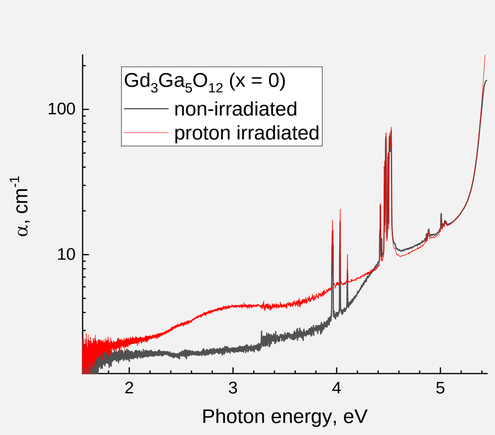
1. Non irradiated crystals

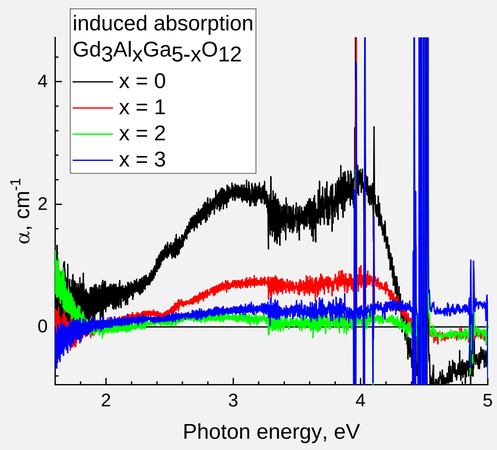


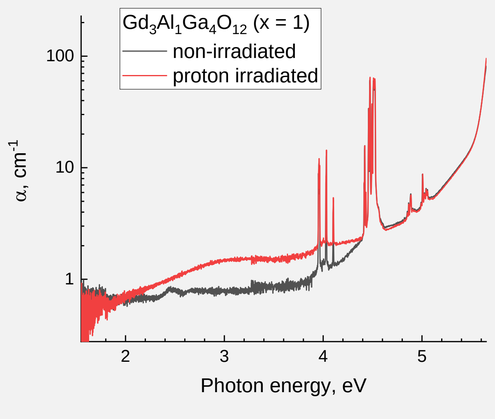
Absorption spectra of $Gd_3Al_xGa_{5-x}O_{12}$, T = 300 K. Tauc plot and optical band gap approximation are presented in the inset.

- **Absorption spectra were corrected using Fresnel formulas on reflection losses considering multiple reflections between crystal surfaces.**
- **Sets of narrow lines at 3.95-4.11 eV, 4.40-4.55 eV and 4.85-5.05 eV are related to transitions from the ground $^8S_{7/2}$ term to ^6P_J, ^6I_J and ^6D_J terms within Gd^{3+} ions, respectively.**
- **The rise of absorption coefficient at E > 5.1 eV is related to the fundamental absorption edge. The position of the fundamental absorption edge shifts to the high-energy region with an increase of the fraction of aluminum in the crystal.**
- **The optical band gap (E_g^{opt}) values were derived from the Tauc plot approximation. E_g^{opt} were determined as 5.38, 5.63, 5.88 and 6.01 eV for the GAGG crystals with x = 0,1,2,3, respectively.**

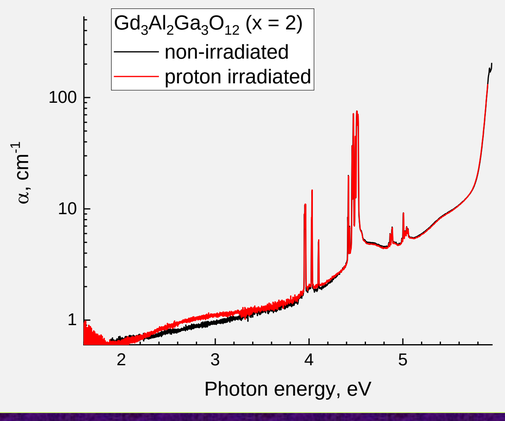
2. Influence of proton irradiation on absorption of GAGG

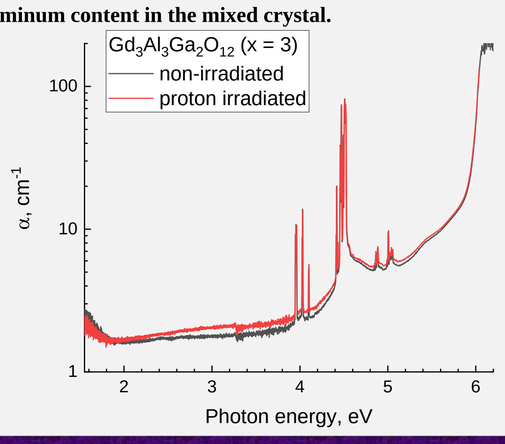






- **$Gd_3Al_xGa_{5-x}O_{12}$ single crystals were irradiated by protons with energy 6.7 MeV for 4 hours at ambient conditions.**
- **Proton beam fluence at the crystals surface was measured using current integrator as $1.4\cdot10^{14}$ protons/cm².**
- **It is shown that the irradiation results in the appearance of additional absorption bands in the transparency region of the crystals. Two bands of induced absorption were detected peaking at 3.0 and 3.9 eV.**
- **The intensity of the bands depends on the crystal's composition. It is shown that the bands intensity decreases with the increase of aluminum content in the mixed crystal.**





Conclusions

- **Proton irradiation results in the appearance of two induced absorption bands peaking at 3.0 and 3.9 eV.**
- **The intensity of the induced absorption bands gradually decreases with the increase of aluminum content in $Gd_3Al_xGa_{5-x}O_{12}$ mixed crystals.**
- **The effect is related to the lower cross-section of interaction with protons in garnet crystals where Ga cations are partially substituted with light Al ones.**