Proton irradiation effects on optical properties of undoped $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0,1,2,3) single crystals

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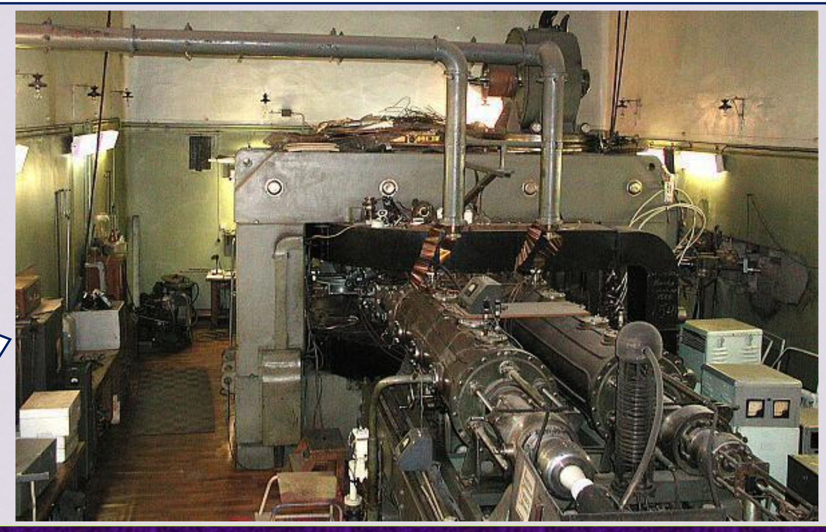
Motivation

The crystals of Ce-doped garnets $Gd_3Al_xGa_{5-x}O_{12}$ (GAGG) attract attention as multipurpose scintillating material due to the combination of high density, chemical stability, high light yield and reasonable energy resolution [P. Lecoq, Nucl. Instr. and Meth. in Phys. Res. A. 809 (2016) 130; M. Korzhik et al., Cryst. Res. Technol. 54 (2019) 1800172.]. Radiation resistance, which is an essential property for scintillators, has been previously studied for the crystals doped with Ce^{3+} ions [V. Alenkov et al., Nucl. Instr. and Meth. in Phys. Res. A. 916 (2019) 226; V.M. Kasimova et al., Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques. 15 (2021) 1259.]. However, the presence of Ce^{3+} - related absorption bands in UV and visible spectral regions hinders observation of induced absorption bands. The studies of undoped crystals allows to avoid this problem and to obtain more reliable data on the parameters of the bands of induced absorption. Here we present the study of the proton radiation effects on the optical transmission of the undoped $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0,1,2,3) garnet crystals.

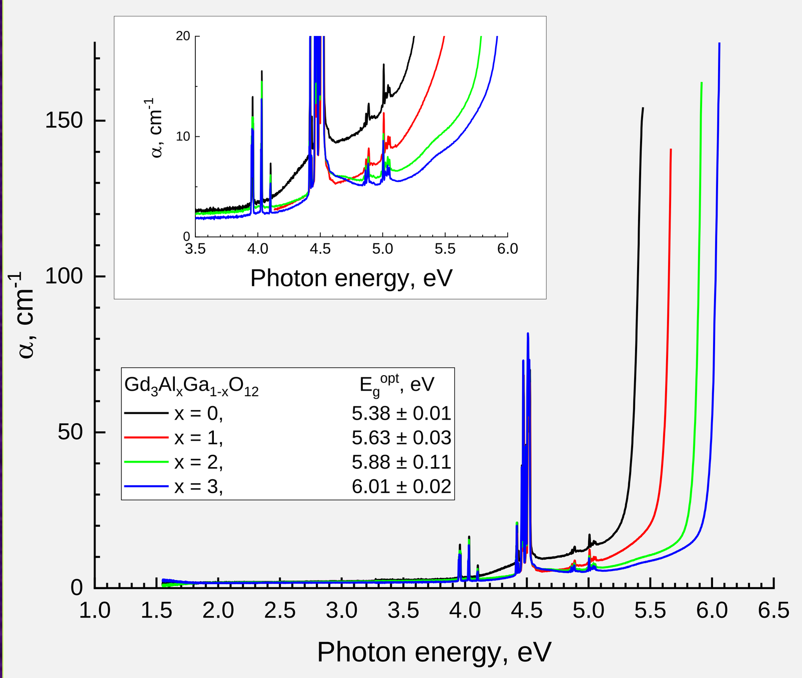
Experimental techniques

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. The crystals were irradiated by protons for two times with a proton beam fluence $1.4 \cdot 10^{14}$ protons/cm^2. The obtained dose was estimated as ~3 MGy each time.

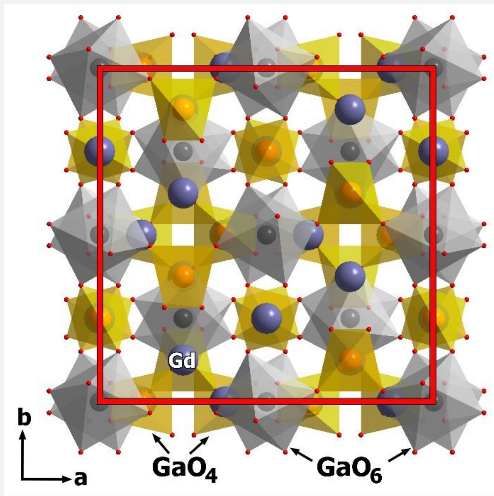
Absorption of non-irradiated crystals



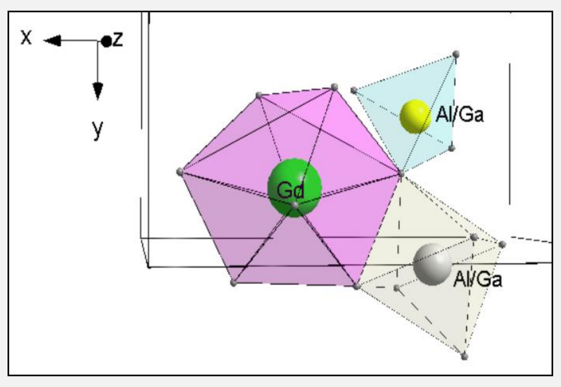
Absorption spectra of $Gd_3Al_xGa_{5-x}O_{12}$, T = 300 K. The enlarged region near bandgap edge is presented in the inset.

- Absorption spectra were corrected using Fresnel formulas on reflection losses considering multiple reflections between surfaces.
- Sets of narrow lines at 3.95-4.11 eV, 4.40-4.55 eV and 4.85-5.05 eV arise due to $^8S_{7/2} \rightarrow {}^6P_J$, ^6I_J and ^6D_J transitions within Gd^{3+} ions.
- The sharp rise of absorption coefficient at E > 5.2 eV is related to the fundamental absorption edge. The edge shifts to the high-energy region with x value (i.e. with aluminum content increase).
- 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 $Gd_3Al_xGa_{5-x}O_{12}$ crystals with x = 0,1,2,3, respectively.
- A broad structureless absorption band below E_g^{opt} is observed for all crystals. This absorption is related to structural defects.
- Evaporation of gallium oxide from the melt results in the formation of oxygen and gallium vacancies as well as related defects (antisite Gd^{3+}_{Ga3+} defects as well as different types of F centers) in $Gd_3Ga_5O_{12}$ crystal. The intensity of the band decreases with x value due to the decrease of gallium content and related defects in the crystal.

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.

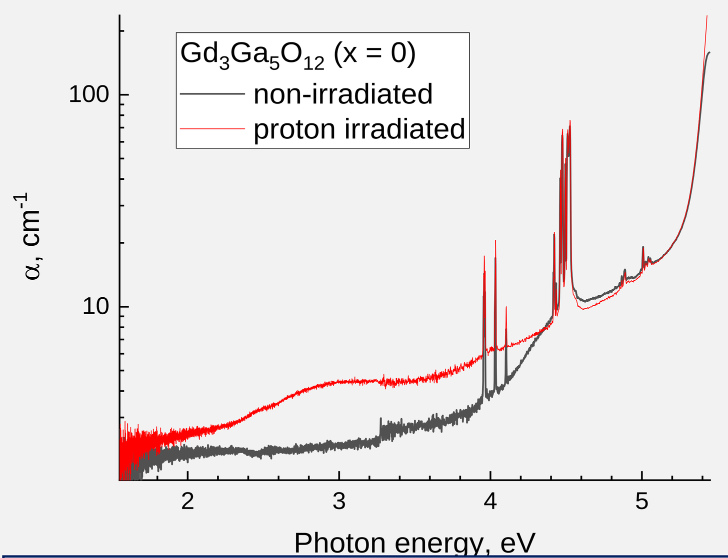


	A – site dodecahedral	B - site octahedral	C - site tetrahedral
$Gd_3(Al,Ga)_5O_{12}$	Gd^{3+} (0.105 nm)	Ga^{3+} (0.062 nm) Al^{3+} (0.054 nm)	Ga^{3+} (0.047 nm) Al^{3+} (0.039 nm)

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

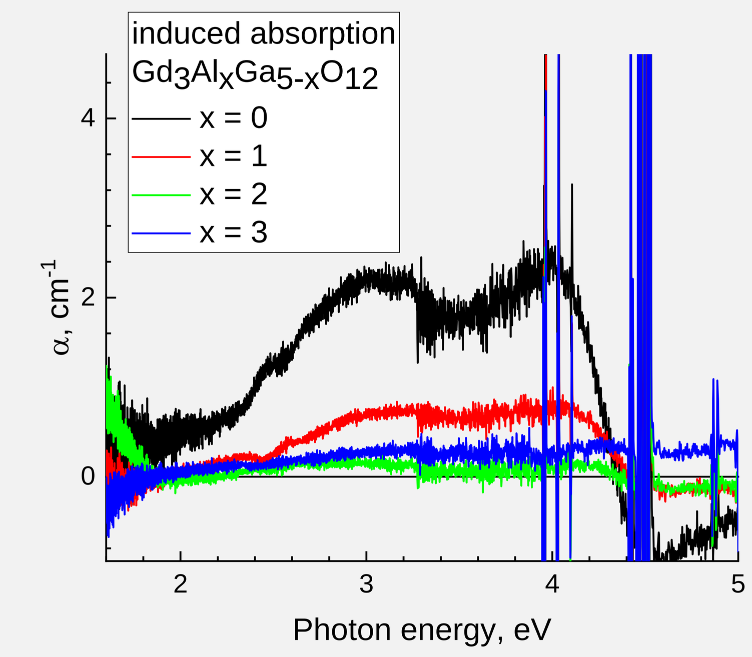
Absorption spectra of irradiated $Gd_3Al_xGa_{5-x}O_{12}$

1. Influence of the single irradiation cycle on absorption of $Gd_3Al_xGa_{5-x}O_{12}$

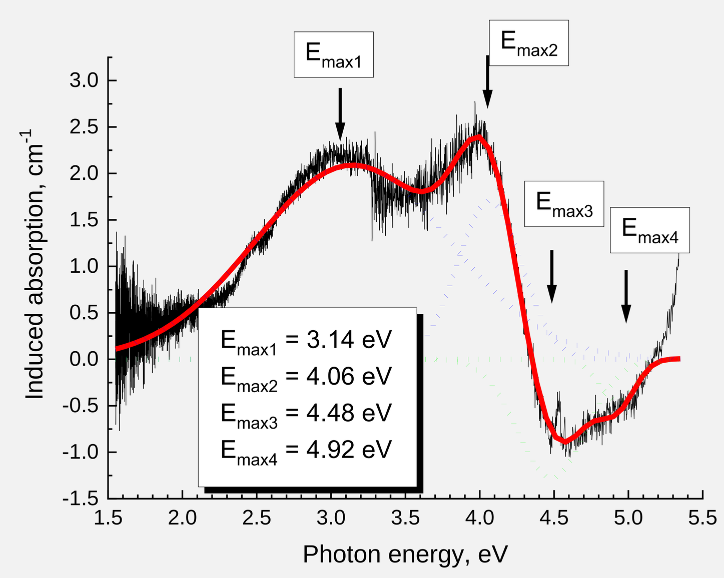


Absorption spectra of $Gd_3Ga_5O_{12}$ crystal before and after proton irradiation.

- Influence of the proton irradiation on the optical absorption is presented for the sample with x = 0. The most pronounced changes has been detected for this sample.
- The irradiation resulted in the appearance of two bands of induced absorption bands in the region 1.5 – 4.3 eV and suppression of two absorption bandsin the region 4.3 – 5.3 eV.
- Redistribution between the absorption bands in irradiated crystal is related to the recharge of the defects, already existing in the crystal.
- We suppose that irradiation results in the excitation of electrons from the valence band, which could be further captured by F centers (one electron at oxygen vacancy) thus forming F^- centers.



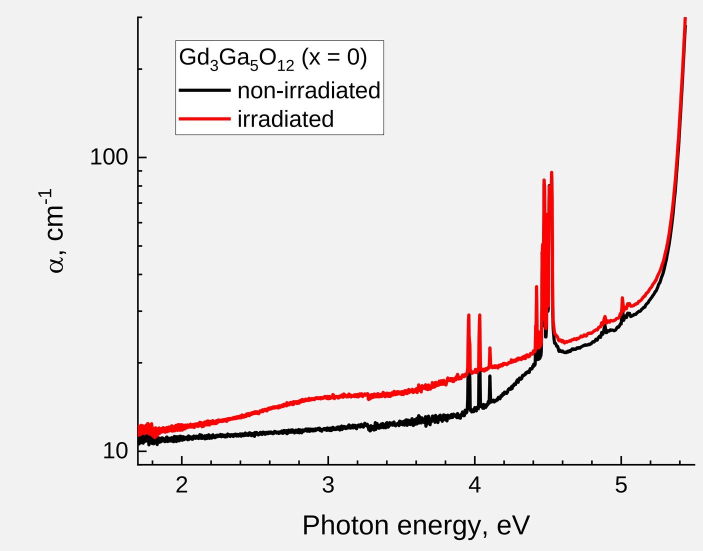
Spectra of induced absorption for $Gd_3Al_xGa_{5-x}O_{12}$ crystals.



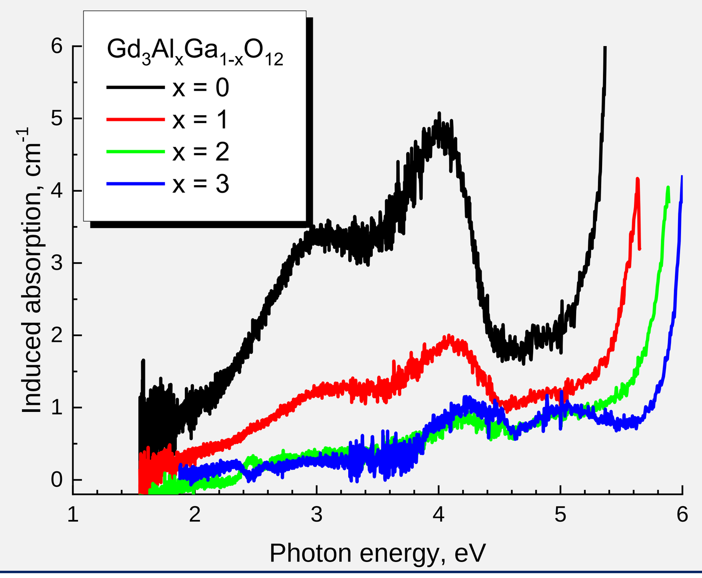
Decomposition of induced absorption spectrum of $Gd_3Ga_5O_{12}$ into Gauss components.

Absorption spectra of irradiated $Gd_3Al_xGa_{5-x}O_{12}$

2. Induced absorption of $Gd_3Al_xGa_{5-x}O_{12}$ after two cycles of proton irradiation

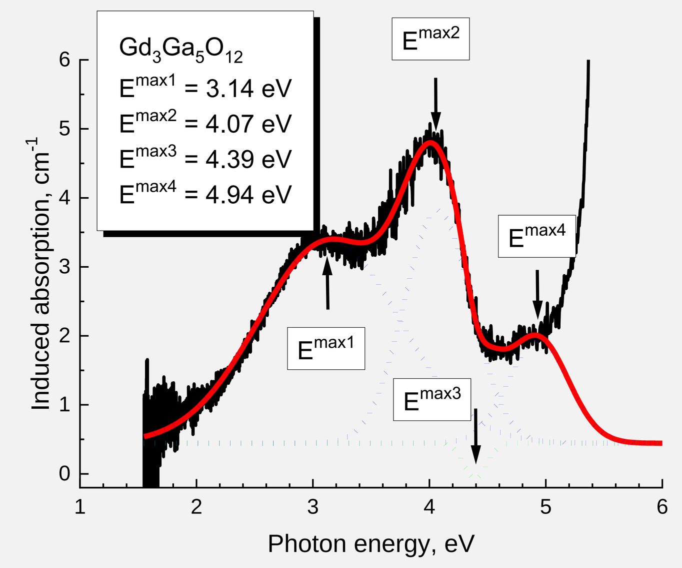


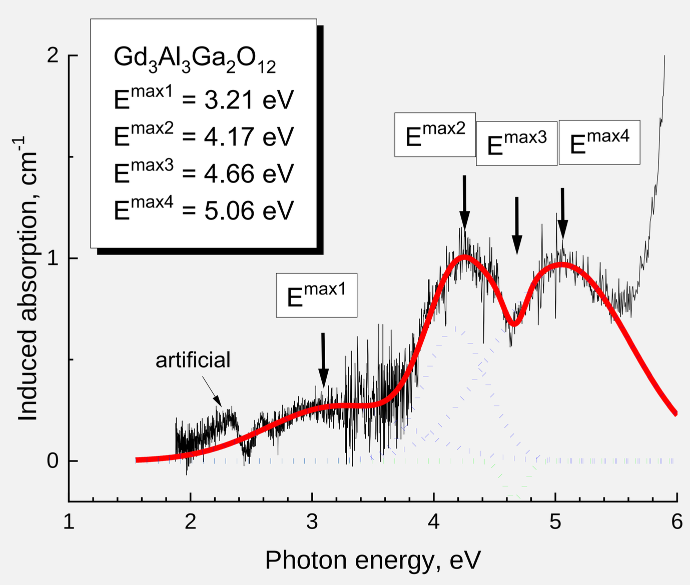
Absorption spectra of $Gd_3Ga_5O_{12}$ crystal before and after proton irradiation.



Spectra of induced absorption for $Gd_3Al_xGa_{5-x}O_{12}$ crystals.

- The increase of irradiation dose results in the increase of garnets absorption in the transparency region from 1.7 eV and up to the fundamental absorption edge.
- The decomposition of induced absorption spectra on Gauss components demonstrates that appearance of additional absorption band peaking around 5 eV is responsible for the increase of absorption in the high energy part of transparency region. The band is attributed to the defects connected with the displacement of ions from lattice sites.
- The induced absorption is most pronounced for the $Gd_3Ga_5O_{12}$ crystal (x = 0) while it decreases with the increase of Al content in the crystal.
- $Gd_3Ga_5O_{12}$ is characterized by the highest concentration of structural defects before radiation. For other crystals the effect is less pronounced and demonstrates the tendency to decrease with the increase of Al content.
- Therefore, we conclude that the radiation damage of $Gd_3Al_xGa_{5-x}O_{12}$ crystals is mainly connected with the defects arising due to gallium oxide evaporation from the melt. Partial substitution of Ga with Al ions doesn't result in appearance of additional bands of induced absorption.





Decomposition of induced absorption spectrum of $Gd_3Al_xGa_{5-x}O_{12}$ (x = 0,3) into Gauss components.

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Conclusions

- Proton irradiation results in the appearance of induced absorption bands peaking at ~3.2, 4.1 and 5.0 eV. Appearance of two former bands is accompanied by the crystal's bleaching and are ascribed to the recharge of F centers. The latter band is ascribed to the displacement defect.
- The intensity of induced absorption is proportional to the Ga content in the crystal. The defects formation in $Gd_3Al_xGa_{5-x}O_{12}$ is connected with evaporation of gallium oxide from the melt.
- Partial substitution of Ga with Al improves radiation hardness of $Gd_3Al_xGa_{5-x}O_{12}$.