Study of optical and luminescence properties of undoped $Gd_3(Ga,Al)_5O_{12}$ scintillating single crystals

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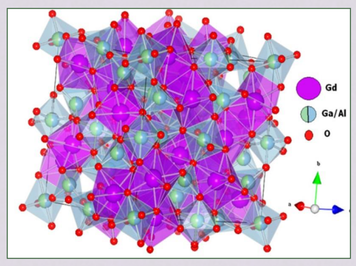
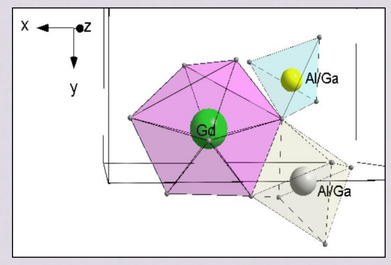
Motivation

The Ce-doped garnet scintillator 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. These crystals attract attention due to the combination of high density, chemical stability, high light yield and good energy resolution. The tailoring of luminescence and scintillation properties of GAGG crystals can be achieved using the method of the bandgap engineering, which consists in gradual variation of substitutional cations concentration. The influence of such variation on optical properties and, in particular, on the bandgap values has been studied previously for the Ce doped GAGG crystals only. However, Ce absorption bands distort the fundamental absorption edge. Therefore, the studies on undoped crystals are required. Here we present the results of the study of the influence of partial substitution of Al for Ga cations on the optical and luminescence characteristics of the undoped $Gd_3Al_xGa_{5-x}O_{12}$ (x = 2 and 3) crystals.

The crystal structure of $Gd_3(Ga,Al)_5O_{12}$



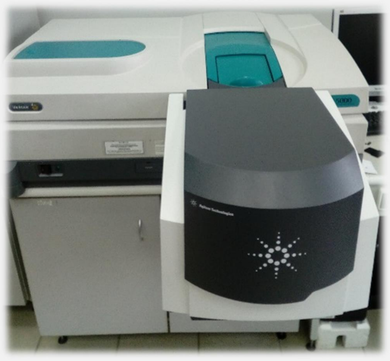
- GAGG has cubic structure with a space group of *Ia3d*;
- The general chemical formula $A_3B_2^{oct}C_3^{tet}O_{12}$ contains three types of oxygen polyhedrons;
- Gd^{3+} occupies dodecahedral sites while Al^{3+} and Ga^{3+} are distributed between octahedral and tetrahedral sites.



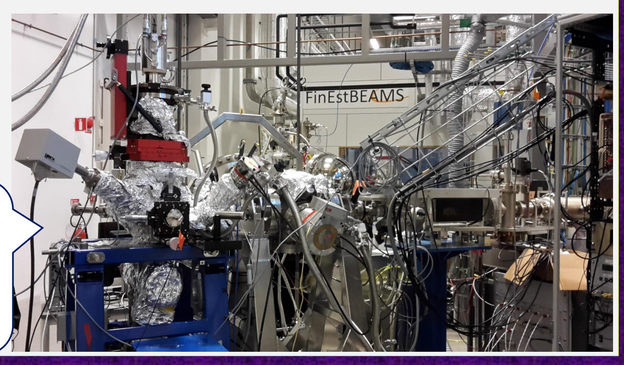
	A – site dodecahedral	B - site octahedral	C - site tetrahedral
$Gd_3(Al,Ga)_5O_{12}$	Gd^{3+} (0.105 nm)	Ga^{3+} (0.062 nm) Al^{3+} (0.054 nm)	Ga^{3+} (0.047 nm) Al^{3+} (0.039 nm)

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

Experimental techniques



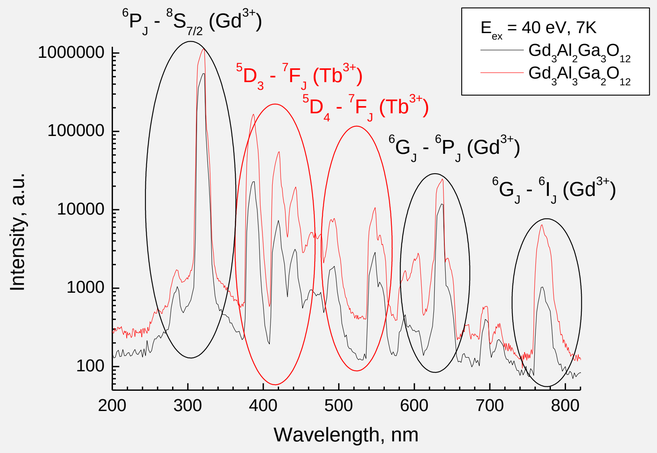
Absorption spectra were measured using an Agilent Technologies Cary-5000 spectrophotometer at 300 K and PerkinElmer Lambda 950 spectrophotometer in temperature region 80-500 K.



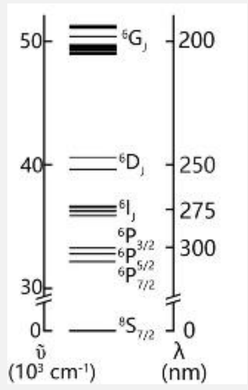
Luminescence excitation and emission spectra under excitation in the UV-VUV region were measured using the photoluminescence endstation of the FinEstBeAMS undulator beamline at the MAX IV synchrotron facility (Lund, Sweden).

Luminescence properties of $Gd_3(Ga,Al)_5O_{12}$

1. Luminescence spectra



Gd^{3+} energy levels

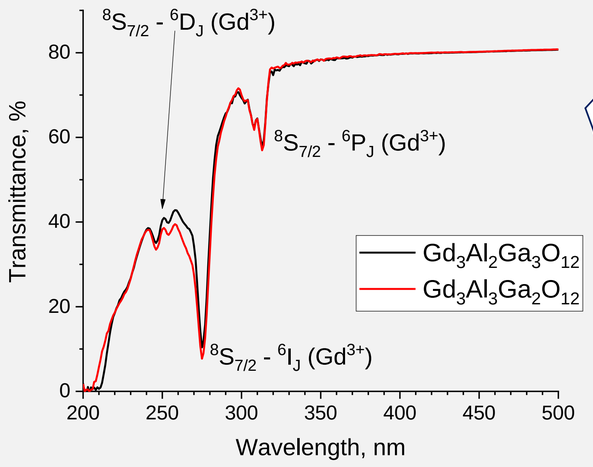


(from https://doi.org/10.1063/1.4976304)

- In the luminescence spectra, narrow emission lines were detected at low temperatures in UV, visible and IR spectral regions and ascribed to the ^6P_J – $^8S_{7/2}$, ^6G_J – ^6P_J and ^6G_J – ^6I_J 4f-4f radiative electron transitions within Gd^{3+} ions.
- Traces of Tb^{3+} impurity results in the emission lines in the spectral region 370-550 nm.
- The Gd^{3+} emission intensity increases with Al concertation.
- The broad intrinsic emission band usually observed in the garnets is quenched in GAGG probably due to the energy transfer to Gd^{3+}.

Optical properties of $Gd_3(Ga,Al)_5O_{12}$

1. Transmission spectra



- The crystals are characterized by high transmission in the transparency region.
- Narrow dips in the spectral regions 310, 275 and 250 nm are connected with electronic transitions from $^8S_{7/2}$ to ^6P_J, ^6I_J and ^6D_J states within Gd^{3+} cations.
- The transparency cutoff is observed at 211 nm for GAGG with x = 2 and 205 nm for x = 3.
- The transparency cutoff is connected with the host absorption. Its shift connected with the bandgap increase with x.

2. Refractive index

- Refractive index was measured by the multi angle spectrophotometry method based on Brewster law:

$$tg\ \varphi_{Br} = n/n_0$$

where n – the refractive index of crystal,
n_0 – the refractive index of air (n_0 = 1),
φ_{Br} – the Brewster angle.

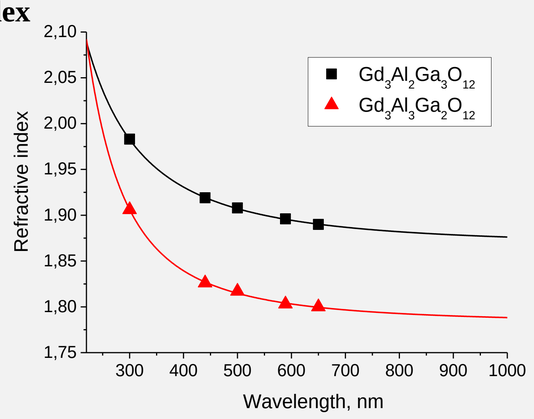
- Results were approximated by the Cauchy equation:

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

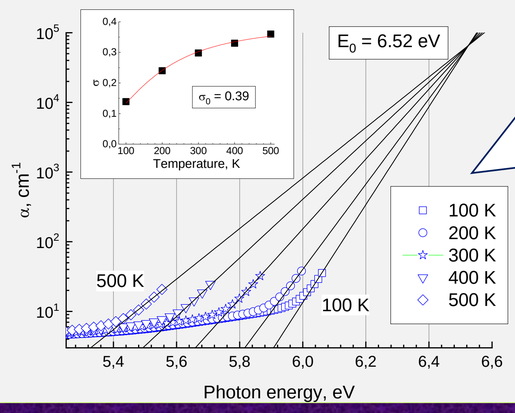
where A, B, C - characteristic constants.

For GAGG with x = 2 A=1.866 B=10167.3 C=30945100
For GAGG with x = 3 A=1.781 B=6862.6 C=396786000

- The refractive index value increases with Ga concentration



3. Temperature dependence of fundamental absorption edge



- The temperature dependence of the fundamental absorption edge was approximated using Urbach formula for GAGG with x = 2.

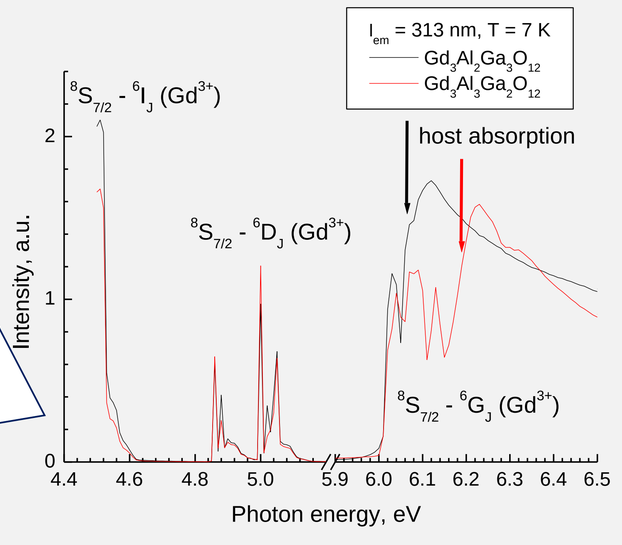
$$\alpha(E) = \alpha_0 exp\left(-\sigma\frac{E_0 - E}{kT}\right)$$

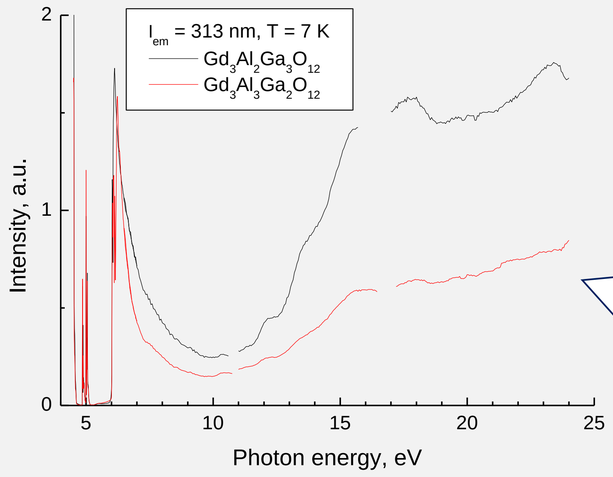
where α_0 and E_0 are the intersection coordinates,
k_B - Boltzmann constant,
T - temperature,
σ - temperature-dependent steepness parameter.

- E_0 = 6.52 eV can be used for the estimation of the bandgap value E_g of the crystal.

2. Gd^{3+} luminescence excitation spectra

- In the excitation spectra, electronic transitions from $^8S_{7/2}$ to ^6P_J, ^6I_J and ^6D_J were observed in crystals transparency region.
- The transitions from $^8S_{7/2}$ to ^6G_J were observed for the GAGG crystals with x = 3, while for the crystal with x = 2 these transitions were enveloped by interband electronic transitions.
- It was shown that the increase of Al content from 2 to 3 in GAGG results in the increase of the bandgap by 0.11 eV.





- In the fundamental absorption region (E_{ex} > E_g) the pronounced decrease of excitation intensity is observed thus demonstrating the exciton type of the energy transfer to Gd^{3+} emission centers.
- The threshold of photon multiplication process was estimated as 11.6 eV for GAGG with x = 2 and 12.8 eV for GAGG with x = 3.

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Conclusions

- Optical and luminescence properties of the undoped $Gd_3Al_xGa_{5-x}O_{12}$ crystals with x = 2 and 3 were studied.
- The refractive indexes were determined as 1.890 (x = 2) and 1.799 (x = 3) at λ = 650 nm.
- The temperature dependence of fundamental absorption edge obeys Urbach rule. The bandgap energy of GAGG with x = 2 was estimated as 6.52 eV while that of GAGG with x = 3 is by 0.11 eV higher.
- The emission from Gd^{3+} cations as well as Tb^{3+} impurity was detected in luminescence spectra.
- The behavior of luminescence excitation spectra indicates exciton type of energy transfer to Gd^{3+} emission centers.