



# Growth and spectroscopy of $Gd_3Ga_3Al_2O_{12}$ (GGAG) and evidence of multisite positions of $Sm^{3+}$ ions in solid solution matrix



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## ABSTRACT

Single crystal of  $Gd_3Ga_3Al_2O_{12}$  (GGAG) doped with 1 at.%  $Sm^{3+}$  was fabricated by the Czochralski method. Optical absorption and emission spectra as well as luminescence decay curves for this crystal was recorded at different temperatures ranging from 5 K to 300 K. The energies of the crystal field sublevels of selected multiplets were determined based on optical spectra recorded at  $T = 5$  K. It has been found that widths of emission spectral lines related to transitions between individual crystal field levels of multiplets are stable up to 100 K, then new Stark component of higher the  $^4G_{5/2}$  multiplets starts to appear in the spectrum. The spectral widths (FWHM) are in the range  $7-30\text{ cm}^{-1}$  what is caused with solid solution composition of the crystal. Five local positions of the  $Sm^{3+}$  have been found in this material. Judd-Ofelt calculation of branching ratios has been done. The color of luminescence is orange-red with CIE coordinates as  $x = 0.606$  and  $y = 0.393$  and the total efficiency 45%.

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## 1. Introduction

Garnet crystal are attractive materials since at 60's the laser action in matrixes doped with  $Nd^{3+}$  of  $Y_3Al_5O_{12}$  (YAG),  $Y_3Ga_5O_{12}$  (YGG) and  $Gd_3Ga_5O_{12}$  (GGG) has been observed [1]. The threshold has been determined to be 2, 250 i 350 J, respectively. Latter other garnet  $Lu_3Al_5O_{12}$  (LuAG) has been considered as a laser host [2].

Besides  $Nd^{3+}$  activator a couple of papers has been appeared on  $Ce^{3+}$  due to  $Ce^{3+}$  ion in garnets is very effective converter of excitation quantum into visible emission. The earliest data on  $Ce^{3+}$  in YAG has come from the 60's, also [3]. Then the information about the efficiency of  $Ce^{3+}$  in YAG (25000 photons per MeV) [4] and  $Pr^{3+}$  in LuAG (20000 photons per MeV) [5] has been given. That is unclearly less than it is possible based on theoretical Bertram-Lempicki [6] equation (60000 phonons per MeV). This phenomenon of  $Ce^{3+}$  quenching has been assigned to defects such as cation and ligand vacancies, antisites and mix  $Ce^{3+}/Ce^{4+}$  oxidation states

[7–11]. Completely quenching of  $Ce^{3+}$  emission in  $Y_3Ga_5O_{12}$  and  $Gd_3Ga_5O_{12}$  is still thought-provoking [12–14]. The knowledge about spectroscopic properties of other ions than  $Ce^{3+}$  or  $Pr^{3+}$  is poor. Up to our knowledge there is only one publication about  $Nd^{3+}$  properties in GGAG [15]. However, it should be noted that structure and luminescent properties of other garnets are under intensive study until now [16–22].

In the past the interest in  $Sm^{3+}$ -doped luminescent materials was marginal owing to the insufficient absorption properties for optical pumping with classical lamps. This shortcoming can be overcome at near future owing to rapid development of blue emitting laser diodes with quite high power [23]. The promising luminescence features of single crystals containing  $Sm^{3+}$  admixture were documented [24–26]. The large energy gap between the metastable level  $^4G_{5/2}$  and a next lower-lying state results in low contribution of nonradiative multiphonon relaxation and thereby in efficient yellow-red luminescence. In addition, it has been shown that this emission can be enhanced in numerous inorganic materials applying the europium-samarium energy transfer [27–29]. The preliminary spectroscopic investigations of  $Sm^{3+}$  doped GGG and (Ca, Mg, Zr)GGG crystals grown by Czochralski technique have been reported [30,31]. In particular, absorption and emission spectra were measured at room temperature and analyzed in the framework of the Judd-Ofelt theory. High absorption cross-section

Abbreviations: LED, light-emitting diode; YAG,  $Y_3Al_5O_{12}$ ; YGG,  $Y_3Ga_5O_{12}$ ; LuAG,  $Lu_3Al_5O_{12}$ ; GGG,  $Gd_3Ga_5O_{12}$ ; GGAG,  $Gd_3Ga_2Al_2O_{12}$ ; JO, Judd-Ofelt; 4N5, 99.995%; 5N, 99.999%; FWHM, full width at half maximum; CIE, Commission Internationale de l'Éclairage; RMS, root-mean-square; ED, electric dipole; MD, magnetic dipole.

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at 405.9 nm and high quantum efficiency of the luminescence from metastable level were estimated. The emission cross-section of  $3.18 \times 10^{-21} \text{ cm}^2$  at 613 nm related to the transition  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$  was found for GGG:Sm crystal. Considerably lower value of emission cross-section amounting to  $4.28 \times 10^{-22} \text{ cm}^2$  was estimated for (Ca, Mg, Zr):GGG crystal.

Intention of the present work is a quest to get a new efficient red phosphor able to be excited with commercial ~405 nm sources. Beside this, we try to obtain data to get new information relevant to luminescence phenomena in  $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$  crystals doped with  $\text{Sm}^{3+}$ , that might help to understand nature of narrow lowering of quantum yield of Ce doped GGAG at about 150 K [32], encompassing their spectral features and excited state relaxation dynamics.

## 2. Experimental

Good quality single crystal of  $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ : doped with 1 at.% of  $\text{Sm}^{3+}$  was grown by the Czochralski method using a Malvern MSR4 puller with automatic diameter control based on weighing the crucible. As starting materials  $\text{Gd}_2\text{O}_3$  (4N),  $\text{Al}_2\text{O}_3$  (4N5) and  $\text{Ga}_2\text{O}_3$  (5N) were used. Substrates were dried 1000 °C for 6 h prior to weighing and mixing with suitable admixtures of dopant oxides. Powders were formed into pellets under 200 kPa pressure and calcinated at 1500 °C for 6 h in air. Such a prepared material was put into iridium crucible of 40 mm in diameter, shielded with  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  ceramic insulation, and molten in ambient ( $\text{N}_2$ ) atmosphere. Single crystals were grown on the  $\langle 111 \rangle$  oriented seed with a pulling rate of 2.5 mm/h and a rotation speed of 20 rpm. Obtained single crystal with 20 mm of the diameter and 60 mm in length was transparent. The as-grown crystal demonstrated good optical quality with no visible defects. The polished sample in the form of rectangular plate several millimeters thick was prepared for optical measurements, see Fig. 1.

The absorption spectra were measured with a Varian Model 5E UV-VIS-NIR spectrophotometer. High-resolution emission spectra were recorded with an experimental system consisting of a Dongwoo Optron DM 158i excitation monochromator and DM711 emission monochromator having 750 mm focal length. A “405 OBIS” 50 mW diode laser emitting at 403 nm was used to excite the sample. Spectral resolution (FWHM) of DM711 emission monochromator was  $1 \text{ cm}^{-1}$ . An ozone-free Xenon lamp DL 180-Xe was utilized as an excitation source. The Continuum Surelite I optical parametric oscillator (OPO) pumped by a third harmonic of Nd:YAG laser and a Tektronix Model TDS 3052 digital oscilloscope was used to record the luminescence decay curves. For low-temperature measurements, a sample was installed in a continuous flow liquid helium cryostat Oxford Instruments equipped with a temperature

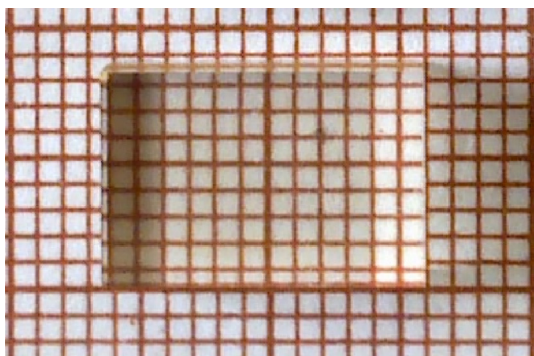


Fig. 1. Polished sample of  $4 \times 8 \times 12 \text{ mm}$  GGAG:Sm 1 at.% used for experiments.

controller. The luminescence branching ratios and quantum efficiency were measured with Hamamatsu integrated sphere system C9920-02G. Judd-Ofelt intensity parameters were determined with an own Fortran based software.

## 3. Results and discussion

$\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$  (GGAG) crystal belongs to cubic garnet system with  $Ia-3d$  space group such as the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  one [33]. In this system three different types of sites are available.  $\text{Gd}^{3+}$  ions enter into dodecahedral positions, surrounded by 8 oxygens (positions 24c in Wyckoff notation) while  $\text{Ga}^{3+}$  and  $\text{Al}^{3+}$  occupies tetrahedral (24d) and octahedral (16a) positions surrounded by 4 and 6 oxygen ions respectively. Unit cell is characterized by the following parameters  $a \approx 12.23\text{--}12.24 \text{ \AA}$  [16],  $Z = 8$ ,  $d = 6.63 \text{ g/cm}^3$ , and samarium concentration 0.215 M.

Incorporated samarium ions should mainly substitute gadolinium ions and owing to very small difference in radii of the two ions the crystal structure should be not distorted even when the doping level is high. All optical spectra in this system are related to intra-configuration transitions within the  $4f^7$  configuration of  $\text{Sm}^{3+}$ . Fig. 2 presents survey absorption spectrum of the GGAG:1 at.% Sm crystal measured at 5 and 300 K.

At such a low temperature spectral lines are related to transitions from the lowest energy Stark component of  ${}^6\text{H}_{5/2}$  ground state to higher-lying multiplets of  $\text{Sm}^{3+}$ . It can be seen in Fig. 2 that there are two groups of spectral lines separated by relatively large energy gap. Referring to energy level diagram of  $\text{Sm}^{3+}$  the absorption lines in infrared region are assigned to transitions terminating on low energy multiplets of  ${}^6\text{H}$  and  ${}^6\text{F}$  sextet terms whereas absorption lines in the visible and UV region are due to transitions to higher energy multiplets of  ${}^4\text{F}$ ,  ${}^4\text{G}$ ,  ${}^4\text{H}$ ,  ${}^4\text{I}$ ,  ${}^4\text{K}$ ,  ${}^4\text{L}$ ,  ${}^4\text{M}$  quartets terms. The energy gap between the two groups of multiplets corresponds to energy distance between the highest energy crystal field component of the  ${}^6\text{F}_{11/2}$  state and lowest energy Stark sublevel of  ${}^4\text{G}_{5/2}$  multiplet. In GGAG:Sm system it is about  $7000 \text{ cm}^{-1}$ . Assignment of well separated absorption lines of  $\text{Sm}^{3+}$  in infrared region is quite straightforward but it is problematic for transitions within visible and UV region where energy distances between multiplets are frequently lower than crystal field splitting of individual multiplets.

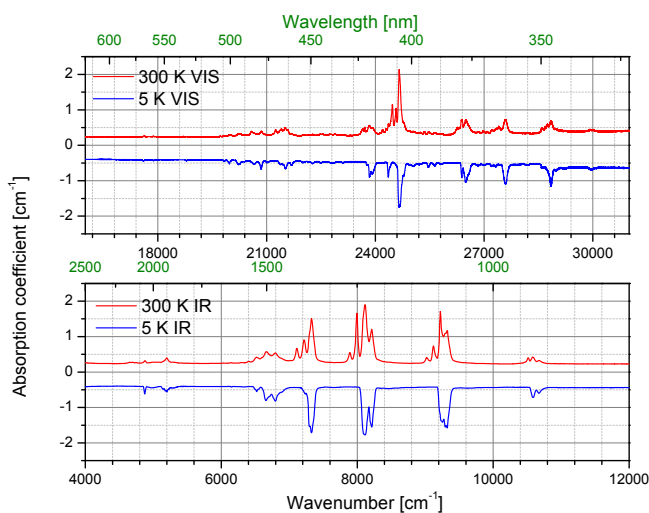


Fig. 2. Absorption spectra of  $\text{Sm}^{3+}$  in GGAG recorded at 5 and 300 K. The assignment of observed multiplets is given at Table 1. The room temperature spectra are inverted. In green the wavelength in nm are given for better clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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