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The temperature dependence studies of rare-earth (Dy^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+}) activated $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ garnet single crystals

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ABSTRACT

The luminescence properties of the Dy^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+} activated $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ (GGAG) single crystals were investigated as a function of temperature. The photoluminescence excitation, emission and decay kinetic analysis revealed an efficient energy transfer from Gd^{3+} ions towards all the Dy^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+} activators. The intensity ratio between electric dipole and magnetic dipole emission transitions in activator's ions suggested a high homogeneity of the host lattice grown by Czochralski technique. Only the $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystal activated with Dy^{3+} ions exhibited a stable luminescence up to 800 K. The Sm^{3+} , Eu^{3+} and Tb^{3+} doped $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystals showed the onset of the thermal quenching of luminescence at lower temperatures. We proposed three different models, very well-known from the literature, to explain the mechanisms responsible for thermal quenching of activator's luminescence in $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystal.

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1. Introduction

Rare-earth aluminum garnets, having a general formula of $\text{RE}_3\text{Al}_5\text{O}_{12}$ (REAG, RE=lanthanide and Y), are an important family of multi-functional materials. The YAG might be the best known garnet compound owing to its excellent chemical stability, high creep resistance, optical isotropy and particularly the ability to accept various trivalent RE^{3+} for diverse optical functionalities. In the bulk form, the YAG: Nd^{3+} single crystal is one of the most widely used solid laser material since its discovery in the 1960s [1]. However, soon the potential of Ce^{3+} doped YAG single crystal for fast scintillators was realized [2]. Cerium activated YAG and LuAG are well-known scintillators, where the former was widely applied a time ago in the cathodoluminescent detectors in electron microscopy [2], and the latter has undergone an intense research and development in the past decade [3]. Recently, a high quality Pr^{3+} activated YAG single crystal has shown an excellent scintillation properties [4], and the Pr^{3+} doped LuAG was also announced as a fast and efficient scintillator [5]. The YAG: Ho^{3+} and YAG: Er^{3+} are an important infrared solid laser materials for medical surgery [6]. In the powder form, RE-activated (Ce^{3+} , Eu^{3+} , Tb^{3+} etc.) YAG is being widely studied and used as a phosphor for

fluorescent lamps, field emission displays and white LEDs [7,8]. The $\text{Y}_3\text{Al}_5\text{O}_{12}$ activated with Dy^{3+} is one of the candidates for thermographic phosphors that can be used for simultaneous non-intrusive measurement of the temperature and velocity fields in a high temperature flows of the combustion systems [9,10]. In the REAG host lattice, the rare-earth occupies a dodecahedral site with eightfold oxygen coordination, two of the five aluminum cations occupy octahedral sites and three occupy tetrahedral sites. The rare earth site can be replaced by the smaller Lu or the larger Gd or La ions, and Al can be replaced by the larger Ga^{3+} or the even Sc^{3+} . Two Al^{3+} can also be replaced by one Mg^{2+} plus one Si^{4+} or Ge^{4+} while maintaining the garnet crystal structure type, and many others substitution are possible [11]. The very wide solid solution compositional variation enables optimization of properties. For example, the crystal field interaction and the red shift can be manipulated enabling color tuning of emission [12]. In recent years, mainly Pr^{3+} and Ce^{3+} activated $(\text{Y,Gd})_3(\text{Ga,Al})_5\text{O}_{12}$ crystals have been intensively studied for application as a scintillating materials [3,12]. Interestingly, such host lattice doped with the other RE ions has been much less explored. However, GGAG material may hold a number of merits for optical applications: (i) the intrinsic $^8\text{S}_{7/2} \rightarrow ^6\text{I}_j$ excitation transition of Gd^{3+} (usually centered at ~ 275 nm) can be utilized as a new excitation source for some types of RE activators, and enhanced luminescence may also be attained via an efficient energy transfer from Gd towards activators [8], (ii) the GGAG host lattice is more covalent than YAG due to lower electronegativity of Gd^{3+} ($\chi=1.20$) than Y^{3+}

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($\chi=1.22$), which may produce a new emission features and result in improved emission intensity.

In this work we characterized in detail the effect of temperature on the luminescence properties of Dy^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+} ions in $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystals by absorption, photoluminescence excitation, emission and radioluminescence spectra measurements. Furthermore, the potential of Gd^{3+} as the energy donor is explored and the energy transfer processes between Gd^{3+} and Dy^{3+} , Sm^{3+} , Eu^{3+} as well as Tb^{3+} were reported. To get insight into thermal quenching processes of the activator's luminescence, the measurements of temperature dependence of decay times and emission intensities of Dy^{3+} , Sm^{3+} , Eu^{3+} and Tb^{3+} were performed. The research has shown that only Dy^{3+} ions exhibits stable luminescence up to 800 K. To explain the mechanisms responsible for the thermal quenching of luminescence of the others activators (Sm^{3+} , Eu^{3+} and Tb^{3+}), three different models from literature were applied.

2. Experimental methods

GGAG single crystals were grown by the Czochralski technique [13], with growth velocities at 1.4 mm/h (between 1.1 and 1.7 mm/h). The compositions of starting melts can be expressed by the formula $(\text{Gd}_{1-x}\text{RE}_x)_3\text{Ga}_{2.9}\text{Al}_{2.1}\text{O}_{12}$. For Eu and Tb was $x=0.01$, for Sm and Dy it was 0.005. Based on microprobe analyses the following values of the distribution coefficients of the four admixtures in the GGAG crystals have been found: $k(\text{Sm})=0.64$, $k(\text{Eu})=0.80$, $k(\text{Tb})=1.25$ and $k(\text{Dy})=1.07$. Polished plates of 12.8 mm \times 1.1 mm cut from the parent rods were used for all the measurements. The absorption spectra of single crystals were measured by the Shimadzu 3101 PC spectrometer in the 200–800 nm spectral range. The radioluminescence spectra were measured at room temperature. The PL decay kinetics and photoluminescence excitation and emission spectra were measured in the temperature interval 77–800 K using the bath liquid nitrogen cryostat Janis Model VPF-800. The custom made 5000M Horiba Jobin Yvon fluorescence spectrometer was used in all experiments. In the steady state photoluminescence and radioluminescence spectra measurements, the samples were excited by deuterium lamp (Heraeus GmbH) and X-ray (40 kV, 15 mA) tube (Seifert GmbH), respectively. All spectra were corrected for the spectral distortions due to the setup. Spectral resolution used in the absorption, photoluminescence excitation and emission and radioluminescence spectra measurements was 1, 4, 4 and 8 nm, respectively. In the decay kinetics measurements, the microsecond xenon flash lamp was used as an excitation source. The signal was recorded by means of multichannel scaling method. True photoluminescence decay times were obtained using the convolution of the instrumental response function with an exponential function and the least-square-sum-based fitting program (Spectra Solve software package).

3. Results and discussion

3.1. $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}:\text{Dy}^{3+}$ 0.5%

Fig. 1 compares the room temperature (RT) absorption spectra of the undoped and Dy^{3+} doped $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystals. Some interesting differences are observed. In the undoped sample a strong absorption starting from 210 nm is ascribed to the absorption of the host lattice edge (HL). Interestingly, in the Dy^{3+} activated sample such strong absorption is significantly shifted towards lower energy and begins at 230 nm. Such difference

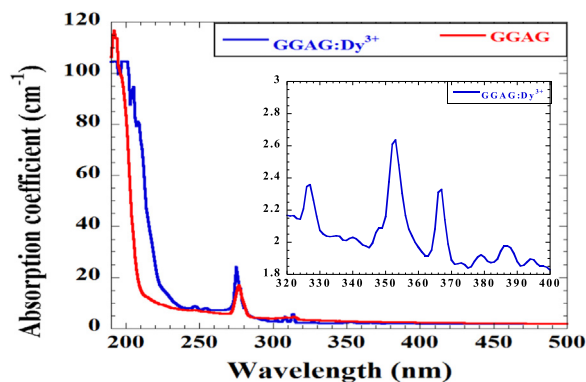


Fig. 1. Absorption spectra of the undoped and Dy^{3+} doped $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ (GGAG) single crystals. Dy^{3+} concentration in the sample is 0.5 mol %. Inset shows enlarged absorption spectrum between 320 and 400 nm.

Table 1

Summary of the absorption (excitation) transitions and peak positions of the Gd^{3+} and Dy^{3+} ions in $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystal.

Ln^{3+} ion	Absorption transition	Peak position [nm]
Gd^{3+}	$^8\text{S}_{7/2} \rightarrow ^6\text{D}_J$	~240, 246
	$^8\text{S}_{7/2} \rightarrow ^6\text{F}_J$	~270
Dy^{3+}	$^8\text{S}_{7/2} \rightarrow ^6\text{P}_J$	~295–308
	$^6\text{H}_{15/2} \rightarrow ^6\text{P}_{3/2}$	~320
	$^6\text{H}_{15/2} \rightarrow ^4\text{I}_{11/2} + ^4\text{M}_{15/2} + ^6\text{P}_{7/2}$	~348
	$^6\text{H}_{15/2} \rightarrow ^4\text{P}_{3/2} + ^6\text{P}_{3/2,5/2}$	~360
	$^6\text{H}_{15/2} \rightarrow ^4\text{I}_{13/2} + ^4\text{F}_{7/2} + ^4\text{K}_{17/2} + ^4\text{M}_{19/2}$	~374–389
	$^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2} + ^4\text{G}_{11/2} + ^4\text{M}_{21/2}$	~410–460

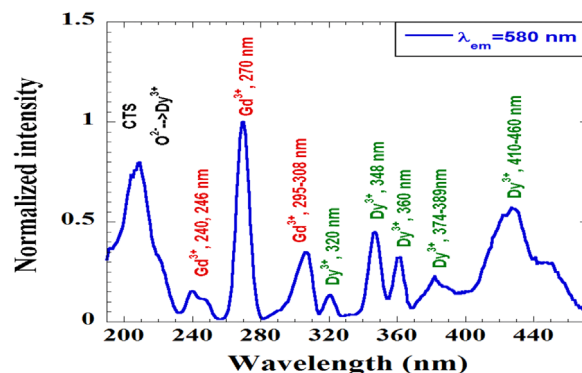


Fig. 2. Room temperature excitation spectrum of the Dy^{3+} luminescence at 580 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) in $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystal.

suggests that the onset of intense absorption at 230 nm in the Dy^{3+} activated sample belongs to $\text{O}^{2-} \rightarrow \text{Dy}^{3+}$ charge transfer (CT) transition. Sharp absorption lines observed in the spectral range from 240 to 313 nm, in both spectra belong to Gd^{3+} ion, whereas very weak absorption peaks between 320 and 400 nm, in the Dy^{3+} activated sample, belong to Dy^{3+} ion [8,14,15], see Table 1. There are no absorption lines within the visible range primarily due to 7500 cm^{-1} energy gap between $^6\text{F}_{3/2}$ (13,366 cm^{-1}) and $^4\text{F}_{9/2}$ (20,860 cm^{-1}) levels of Dy^{3+} . The normalized RT excitation spectrum of Dy^{3+} emission at 580 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ emission transition) in $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ single crystal is depicted in Fig. 2. The spectrum consists of a broad excitation band between 190 and 230 nm with maximum at 210 nm, which belongs to the $\text{O}^{2-} \rightarrow \text{Dy}^{3+}$ CT transition [16], which is consistent with the absorption spectrum, see Fig. 1. The sharp lines between 230 and 313 nm

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