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Study of the luminescence of Eu^{2+} and Eu^{3+} states in $Ca_3Ga_2Ge_3O_{12}$:Eu garnet using synchrotron radiation excitation

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ABSTRACT

The work is dedicated to the investigation of Eu^{2+} and Eu^{3+} luminescence centers in the $Ca_3Ga_2Ge_3O_{12}$ garnet using synchrotron radiation excitation. The luminescence of Eu^{2+} and Eu^{3+} states was observed in the emission spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics under excitation with energies in the exciton range and the range above band gap of this garnet. The luminescence of Eu^{2+} ions $Ca_3Ga_2Ge_3O_{12}$ host is observed in the band peaked at 450–460 nm with decay time in the ten ns range and excited in the two wide bands peaked at 5.04 and 6.05 eV, related to the allowed 4f-5d transitions of Eu^{2+} ions. The Eu^{3+} luminescence can be excited via the Eu^{2+} luminescence. We have also found the energies of formation of excitons bound with Eu^{2+} and Eu^{3+} ions in $Ca_3Ga_2Ge_3O_{12}$, being equal to 7.64 and 6.95 eV, respectively, and the onset of interband transitions in this garnet which is equal to 7.83 eV at 8 K. Strong increase of the luminescence intensity of Eu^{2+} and Eu^{3+} centers is observed under excitation above 21 eV due to multiplication of electronic excitation in $Ca_3Ga_2Ge_3O_{12}$ host.

1. Introduction

Synthesis and characterization of new efficient phosphors for white light emitting diodes (WLED) are now hot topic in the materials engineering. Such sources consist of a blue LED chip and phosphors converters usually emitting in the yellow-red range [1]. Most of these phosphors absorb and emit light as a result of the inter-configuration 5d-4f transitions in rare-earth (RE) ions, such as Ce3+ or Eu2+ [1,2].

Nowadays, a new class of phosphors based on Ce^{3+} and Eu^{2+} doped $A_3B_2C_3O_{12}$ (A = Ca, Y and rare earth ions; B= Mg, Sc, Al, Ga; C=Si, Ge) mixed garnets was proposed for creation of high-power white LEDs [2–9]. The Ce^{3+} and Eu^{2+} ions can be incorporated into the dodecahedral sites of these garnets without any special charge compensation. Meanwhile, taking into account the fact that both divalent and trivalent cations can be localized at the same dodecahedral sites, the coexistence of both Eu^{3+} and Eu^{2+} ions in the garnets is also available. In this case the occurrence of Eu^{2+}–Eu^{3+} mixed valence pairs should be expected, and the electron exchange transfer between $Eu^{2+}+Eu^{3+}\rightarrow Eu^{3+}+Eu^{2+}$ pairs may occur as well. This process can be referred to as the intervalence charge transfer (IVCT) transitions [10,11] and the IVCT luminescence transitions are not excluded in the mentioned mixed garnets. Thus, in the Ca–Si-Ge based garnets, doped with europium ions, variety of optical centers can be observed, namely, Eu^{2+}, Eu^{3+} and even Eu^{2+} + Eu^{3+} IVCT states.

The aim of this work is investigation of the Eu-related luminescence centers in $Ca_3Ga_2Ge_3O_{12}$ garnet ceramics using synchrotron radiation (SR) excitation. Recent studies of the luminescence properties of undoped as well as Tb^{3+} and Eu^{3+} doped $Ca_3Ga_2Ge_3O_{12}$ garnets were performed using conventional spectroscopic methods [12–15]. Meanwhile, the application of the synchrotron radiation excitation with energy in the 3.7 eV–25 eV range, covered partly the transparence range ($E < 4.0$ eV), the exciton range (4–7 eV) and the range of interband transitions ($E > 7$ eV) of $Ca_3Ga_2Ge_3O_{12}$ host gives the unique possibility of correct investigation of the luminescent properties of the different kinds of dopant in this garnet.

2. $Ca_3Ga_2Ge_3O_{12}$:Eu preparation and experimental technique

Sample of $Ca_3Ga_2Ge_3O_{12}$:Eu (1 at. %) garnet ceramics was prepared from $CaCO_3$ (4 N), Ga_2O_3 (5 N), GeO_2 (5 N) and Eu_2O_3 (5 N) oxides, mixed in the stoichiometric garnet proportion, using solid state ceramic technology at a temperature of 1100 °C in N_2 + H_2 atmosphere. The

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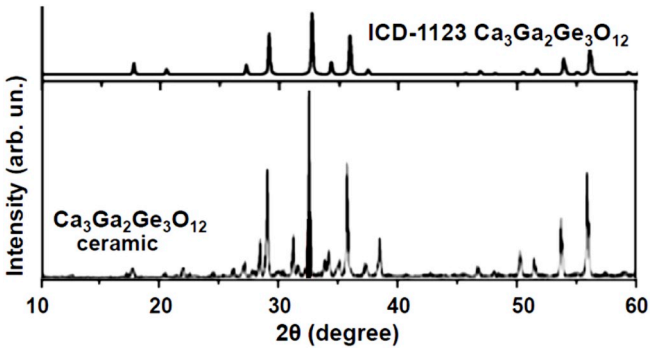

Fig. 1. XRD pattern of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramic sample.

formation of $Ca_3Ga_2Ge_3O_{12}$ phase with a lattice constant of 12.255Å was confirmed by the respective XRD pattern of the ceramic sample, presented in Fig. 1.

The luminescent properties of the $Ca_3Ga_2Ge_3O_{12}$:Eu (1 at %) garnet ceramics were studied using the time-resolved luminescence spectroscopy under excitation by SR at the Superlumi station at DESY (Hamburg, Germany) at 8 K. The emission and excitation spectra were measured with a monochromator ARC and photomultiplier Hamamatsu R6358P in both the integral regime (1.2–100 ns) and in the 1.2–12 ns and 65–100 ns time intervals (fast and slow components, respectively) in the limits of SR pulse with a repetition time of 100 ns. The decay kinetics of the luminescence was measured in the 0–100 ns time range. The excitation spectra were corrected for the spectral dependence and intensity of the excitation energy; the emission spectra were not corrected.

3. Experimental results

3.1. Emission spectra

The initial and normalized **e**mission spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics (Fig. 2a and b, respectively) show the wide Eu^{2+} luminescence band peaked in the 450–459 nm range under excitation with different energies above the band gap at 11.15 eV (curve 1), the exciton range at 7.28 eV (curve 2) and the range of intrinsic Eu^{2+} transition in the UV range at 5.01 eV (curve 3), as well as the two sharp luminescence bands peaked in the 596–599 nm and 710–720 nm ranges related to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+} ions, respectively. Meanwhile, no sign of the Eu^{3+}-Eu^{2+} IVCT transitions was found in the luminescence spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramic.

It is worth to note that some deviation in the position of the Eu^{2+} emission bands in the 450–465 nm range in the normalized spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics under excitation by SR with different energies (Fig. 2b) can be caused by some overlapping of the Eu^{2+} emission band with the emission band of defect related centers peaked approximately at 460 nm at RT [12,13] and is assumed to the luminescence of F^+ centers [12]. Meanwhile, the Eu^{2+} luminescence band $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics and other garnet compounds possesses much wider FWHM of about 1.1 eV [16,17] than that in the case of the emission band of F^+ centers with typical FWHM of about 0.3 eV (for instance. see Ref. [16] and other works [18–20], related to the luminescence of F+ centers luminescence in garnets and other oxide compounds).

3.2. Excitation spectra of Eu^{2+} and Eu^{3+} luminescence

The time–resolved excitation spectra of the Eu^{2+} and Eu^{3+} luminescence in $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics at 8 K under registration of the luminescence at 420 nm (a) and 710 nm (b) are shown in Fig. 3a and Fig. 3b, respectively.

The excitation spectra of the Eu^{2+} luminescence in $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics show the two wide bands in the UV range, peaked at 5.04 and 6.05 eV, related to the characteristic 4f-5d transitions of Eu^{2+} ions in other garnet states [16,17]. Apart from these bands, the excitation spectra of the Eu^{2+} luminescence consist also of the bands at E_{ex} (Eu^{2+}) = 7.64 eV, most probably corresponding to the energy formation of the excitons bound with Eu^{2+} ions [21,22].

The excitation spectra of the Eu^{3+} luminescence in $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics in the 3.7–25 eV range (Fig. 3b) show the several sharp bands with the main peak at 3.87 nm, related to the f-f transitions of Eu^{3+} ions, and the two wide bands, peaked at 4.99 and 5.9 eV, related to the 4f-5d transitions of Eu^{2+} ions. Therefore, the Eu^{3+} luminescence in $Ca_3Ga_2Ge_3O_{12}$ host can be excited via the Eu^{2+} luminescence in the band peaked at 440–450 nm, which overlaps with the respective Eu^{3+} absorption bands in this range. The excitation spectra of the Eu^{3+} luminescence in the exciton range consist of the bands peaked at E_{ex} (Eu^{3+}) = 6.95 and 7.68 eV, most probably corresponding to the energy formation of the excitons bound with Eu^{3+} ions.

The bumps in the excitation spectrum of slow component of the Eu^{2+} and Eu^{3+} luminescence at 7.8 and 7.9 eV, respectively, can be related to the onset of interband transitions E_g in the $Ca_3Ga_2Ge_3O_{12}$ host similarly to other garnets [21,22]. The excitation spectra of the Eu^{2+} and Eu^{3+} luminescence in $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics in the range above the onset of interband transitions of garnet host consist also of the bands peaked at 9.1 and 11.87 and 9.52 and 11.63 eV at 8 K, respectively, which are typical for other garnet compounds [14,16]. In general, taking into account the E (4f-5d Eu^{2+}), E_{ex} (Eu^{2+}), E_{ex} (Eu^{3+}) and E_g values, we can also interpret in more detail the structure of the excitation spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics in the 8–25 eV range in terms of the multiplication of the respective excitonic excitations [21,22]. Namely, the observed several bands in the mentioned range can be related to the multiplication of the corresponding excitation [21] with the energies of nE_{ex} (Eu^{2+}), nE_{ex} (Eu^{3+}) and nE_g, where n = 3 and 4 (Fig. 3a and b).

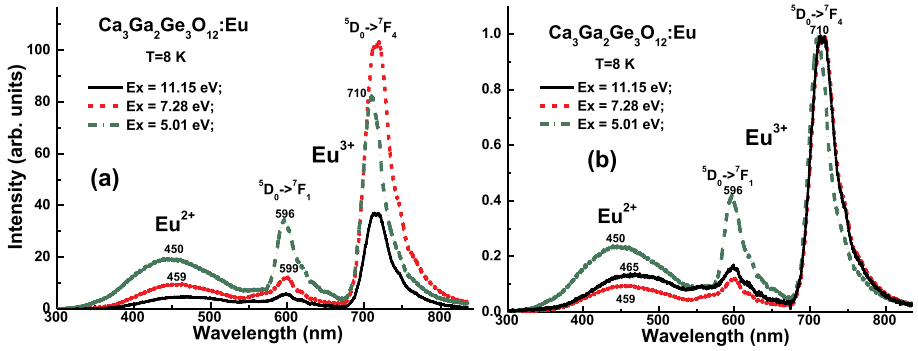

Fig. 2. Initial (a) and normalized (b) emission spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics under excitation by SR with different energies above band gap (1); in exciton range (2) of this garnet and in Eu^{2+} excitation band (3) at 8 K.

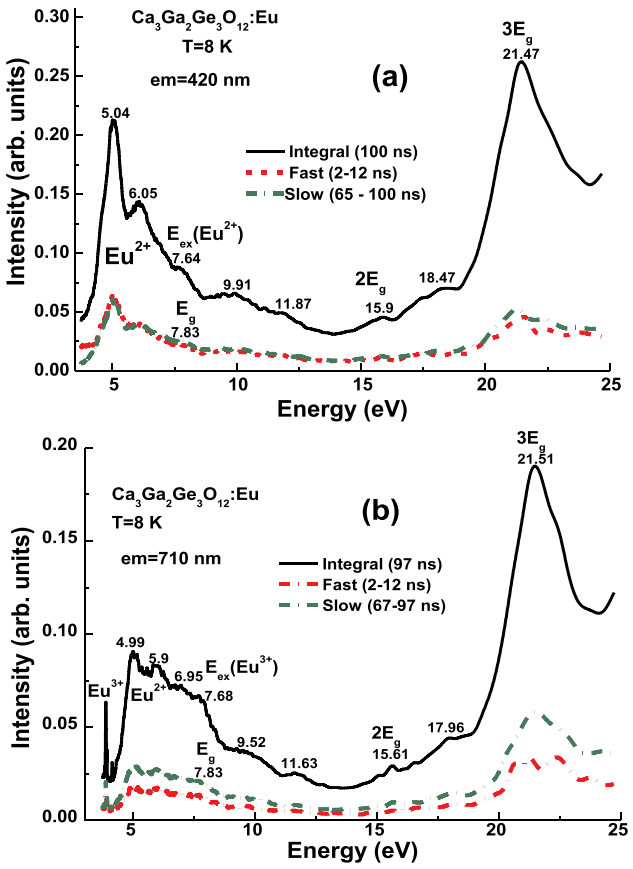

Fig. 3. Excitation spectra of integral (1), fast (2) and slow (3) decay components of Eu^{2+} (a) and Eu^{3+} (b) luminescence in $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics at 8 K under registration of the luminescence at 420 nm (a) and 710 nm (b).

3.3. Decay kinetics of Eu^{2+} and Eu^{3+} luminescence

The decay kinetics of the Eu^{2+} luminescence in $Ca_3Ga_2Ge_3O_{12}$:Eu ceramic at 8 K under excitation with different energies above the band gap; in the exciton range of this garnet and in the Eu^{2+} excitation band is shown in Fig. 4a, curves 1–3, respectively. As can be seen from Fig. 4, all the decay curves are visibly non-exponential, most probably due to the $Eu^{2+}\rightarrow Eu^{3+}$ energy transfer. For this reason, the two-exponential approximation $I = A_i{*}\exp(-t/\tau_i) + \text{const}$; $i = 2$ of the decay curves in Fig. 4 was applied for the estimation of the average decay time of the luminescence. From the respective approximations of the decay curves, we have found the decay times $\tau_1 = 3.62$, 3.85 and 8.56 ns and $\tau_2 = 12.86$, 13.56 ns and 30.6 ns for the cases of excitation at the Eu^{2+} excitation band, exciton range and the range of interband transitions (Fig. 4, curves 3–1, respectively). The shortest decay component of the luminescence in $\tau_1 = 3.6$–3.85 ns range can be partly caused by the overlapping of the Eu^{2+} luminescence with defect centers, namely F^+ centers [17–20]. Meanwhile, the second component of the luminescence in the 12.8–36.6 ns range are more characteristic to the allowed 4f-5d transitions of Eu^{2+} ions in other compounds [16,18].

However, the short decay interval (1.2–95 ns) for the registration of decay kinetics of the luminescence at the Superlumi station makes troubles in the right estimation of the slower decay component of the Eu^{2+} emission. At the same time, the large intensive "pedestal" of the decay curves, especially in the case of excitation with energies above the band gap of $Ca_3Ga_2Ge_3O_{12}$ garnet (Fig. 4a, curve 4), indicates the presence of the third slow decay component whose decay time lies in the hundred ns range.

For confirmation of such a conclusion, we have measured the decay kinetics of the Eu^{2+} luminescence at RT in much wider (up to 500 ns) time interval under excitation by laser diode at 260 nm (Fig. 4b). As can be seen from this figure, the decay curve of the Eu^{2+} luminescence is strongly non-exponential and can be presented by the superposition of the tree exponential components with decay times of 6.4 ns, 21.4 ns and 240 ns. Therefore, the decay kinetics of the Eu^{3+} emission in $Ca_3Ga_2Ge_3O_{12}$ indeed possesses the main slow components with the decay time in the hundred ns range. The non–exponential decay of the Eu^{2+} luminescence (Fig. 4b) can be explained mainly by the energy transfer from Eu^{2+} to Eu^{3+} centers strong overlapping of the Eu^{2+} luminescence band and absorption bands of Eu^{3+} ions and by the temperature quenching of the Eu^{2+} luminescence in the RT range.

4. Conclusions

The investigation of the Eu-related luminescence centers in $Ca_3Ga_2Ge_3O_{12}$ garnet ceramics was performed using synchrotron radiation excitation in the fundamental absorption range of this garnet.

The luminescence of Eu^{2+} and Eu^{3+} states was observed in the emission spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics under excitation with energies in the exciton range and the range above the band gap of this garnet. No luminescence related to the Eu^{3+}-Eu^{2+} IVCT states was found in the emission spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu ceramics.

The luminescence of Eu^{2+} ions in $Ca_3Ga_2Ge_3O_{12}$ garnet is observed in the band peaked in the 450–460 nm range which is excited in the two wide bands peaked at 5.04 and 6.05, related to the allowed 4f-5d transitions of Eu^{3+} ions. The decay time of the Eu^{3+} luminescence in $Ca_3Ga_2Ge_3O_{12}$ host lies in a few hundred ns range. We have found that the Eu^{3+} luminescence can be excited via the Eu^{2+} luminescence. The presence of the Eu^{2+} 4f-5d bands in the excitation spectrum of the Eu^{3+} luminescence and the strongly non-exponential decay kinetics of the

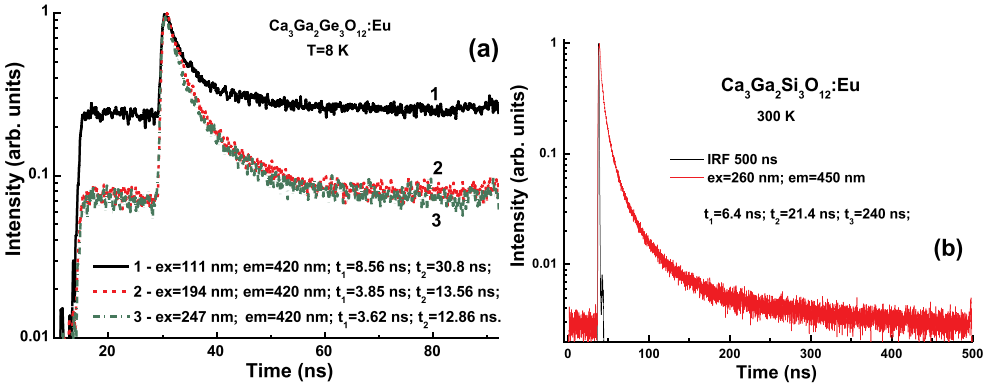

Fig. 4. Decay kinetics of Eu^{2+} luminescence in $Ca_3Ga_2Ge_3O_{12}$:Eu ceramic at 8 K (a) and 300 K (b) under excitation with different energies above band gap (1); in exciton range (2) of this garnet and in Eu^{2+} excitation band (3, 4). IRF - instrumental response function under 260 nm laser excitation.

Eu^{2+} luminescence are an indication of the $Eu^{2+} \rightarrow Eu^{3+}$ energy transfer in $Ca_3Ga_2Ge_3O_{12}$ garnet.

We have also found the energies of formation of the excitons bound with Eu^{2+} and Eu^{3+} ions in $Ca_3Ga_2Ge_3O_{12}$, which are equal to ex (Eu^{2+}) = 7.64 eV and ex (Eu^{3+}) = 6.95 eV, respectively, and the onset of interband transitions in these garnet being equal to 7.83 eV at 8 K. A strong increase of the luminescence intensity of Eu^{2+} and Eu^{3+} centers is observed under excitation above 21 eV due to the multiplication of electronic excitation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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