Spectroscopy and Luminescence Kinetics of Eu^{3+}, Ho^{3+} and Er^{3+} Centres in the Glass With $3CaO$-Ga_2O_3-$3GeO_2$ Composition

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Abstract

The UV-visible optical absorption, luminescence excitation and the emission spectra of Eu^{3+}, Ho^{3+} and Er^{3+} impurity ions in Eu-, Ho- and Er-doped glasses of CaO-Ga_2O_3-GeO_2 system registered at room and liquid-nitrogen temperatures are presented. Luminescence decay curves of the impurity centres in the glass with $Ca_3Ga_2Ge_3O_{12}$ (or $3CaO$-Ga_2O_3-$3GeO_2$) garnet composition are obtained and analysed. The decay curves at the room temperature are described satisfactorily using a two-exponential approximation. We have the characteristic lifetimes $\tau_1 = 0.90$ ms and $\tau_2 = 1.55$ ms for the Eu^{3+} centres ($^5D_0 \rightarrow {}^7F_2$ transition, $\lambda_{max} = 615$ nm), $\tau_1 = 3.9$ μs and $\tau_2 = 7.5$ μs for Ho^{3+} ($^5S_2 \rightarrow {}^5I_8$ transition, $\lambda_{max} = 545$ nm) and $\tau_1 = 10.6$ μs, $\tau_2 = 22.4$ μs and $\tau_1 = 10.7$ μs, $\tau_2 = 25.0$ μs for Er^{3+} ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition, $\lambda_{max} = 555$ nm and $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition, $\lambda_{max} = 545$ nm), respectively. Basing on the optical spectra and the luminescence kinetics analysis for Eu^{3+}, Ho^{3+} and Er^{3+}, the two sites with different local environments are proposed for the rare-earth ions in the $3CaO$-Ga_2O_3-$3GeO_2$ glass surroundings. A possible local structure of the luminescence centres in the glass with $3CaO$-Ga_2O_3-$3GeO_2$ composition is discussed.

1. Introduction

Glasses and crystals doped with rare-earth metal ions are still attractive as effective phosphors and active media for solid-state lasers operating in the visible, near infrared (NIR) and infrared (IR) spectral ranges. In particular, crystals and glasses activated with Eu^{3+} represent promising materials for the efficient "red" phosphors [1,2]. Ho^{3+} and Er^{3+} ions in the oxide compounds exhibit a potential eye-safe laser emission even at the room temperature, with a low threshold action needed for different technical and biomedical applications [3-7]. Moreover, several up-conversion processes can take place within the Ho^{3+} and Er^{3+} energy level scheme, resulting in a visible anti-Stokes luminescence [8,9]. Development of Ho^{3+} and Er^{3+} lasers, amplifiers and up-converters in the optical fibres for telecommunications has given rise to interest in the materials doped with Ho and Er. Particularly, the glasses and disordered crystals activated with Er^{3+} ions have been regarded as promising for developing active elements for the up-converted "green" laser, with a LED-based pumping in the spectral region of $800 \div 970$ nm [10-12].

In view of all these reasons, optical and spectroscopic properties of Eu-, Ho- and Er-

doped crystals and glasses have been extensively investigated during recent years. However, in contrast to what refers to the corresponding crystals, the optical spectra and the peculiarities of incorporation and the ligand fields for the rare-earth impurity ions in complex oxide glasses have remained insufficiently studied. This concerns also Eu-, Ho- and Er-doped glasses of the CaO-Ga_2O_3-GeO_2 system, which are thought to be promising materials for the solid-state lasers and some other applications in optoelectronics. For example, $Ca_3Sc_2Ge_3O_{12}$ garnet host crystals co-doped with Ho^{3+} and Tm^{3+} represent a new potential laser material for the 2 μm region [13].

In the ternary CaO-Ga_2O_3-GeO_2 system, there exist three stable crystalline forms: $Ca_3Ga_2Ge_3O_{12}$ (an ordered garnet structure, space group *Ia3d*), $Ca_3Ga_2Ge_4O_{14}$ (substitutionally disordered Ca-gallogermanate structure, space group *P321*), $Ca_2Ga_2GeO_7$ (gelenite structure, space group $P\bar{4}2_1m$) [14,15] and the corresponding glassy (or vitreous) forms with their stoichiometric compositions similar to that of the crystals [16]. At present, the high-quality glasses with the garnet $Ca_3Ga_2Ge_3O_{12}$ (or $3CaO$-Ga_2O_3-$3GeO_2$) composition doped with the rare-earth metals (Eu, Ho, Er, Nd, Ce, etc.) have been successfully obtained. The optical and spectroscopic properties of Eu-, Ho- and Er-doped glasses with the $3CaO$-Ga_2O_3-$3GeO_2$ compositions have been described for the first time in [17,18,19], though the luminescence kinetics of Eu^{3+}, Ho^{3+} and Er^{3+} luminescence centres has not yet been investigated.

In this paper the luminescence kinetics of Eu^{3+}, Ho^{3+} and Er^{3+} ions in the glass with the garnet $Ca_3Ga_2Ge_3O_{12}$ composition are investigated and analysed and a possible local structure of Eu^{3+}, Ho^{3+} and Er^{3+} luminescence centres in the glass with the $3CaO$-Ga_2O_3-$3GeO_2$ composition is discussed.

2. Experimental details

2.1. Characteristics of samples under investigation

Eu-, Ho- and Er-doped glass samples of high chemical purity and optical quality with the $3CaO$-Ga_2O_3-$3GeO_2$ composition were obtained in corundum crucibles with a conventional high-temperature synthesis technique applied according to [16]. The europium impurity was added to the glass composition as $EuCl_3$ liquid solution (the amount of 0.7 wt %). The holmium and erbium impurities were added to the glass composition as powdered Ho_2O_3 and Er_2O_3 compounds in the amounts of 0.7 wt %. The chemical composition of the obtained samples was controlled with the X-ray microanalysis technique, using the "Camebax" apparatus. The Eu- and Ho-doped glasses with the $3CaO$-Ga_2O_3-$3GeO_2$ compositions were characterised by a lightly yellow colour. The Er-doped glass had a lightly pink colour. All the samples for the optical measurements were cut and polished to the approximate size of 8×4×3 mm^3.

The structure of the samples was investigated using the X-ray scattering and EXAFS (the Extended X-ray Absorption Fine Structure) methods. The Eu-, Ho- and Er-doped samples of the $3CaO$-Ga_2O_3-$3GeO_2$ composition show a typical glassy-like X-ray structure factor, which is quite similar to that of undoped glass of the same composition [20]. Structural investigations of the undoped glasses of CaO-Ga_2O_3-GeO_2 system and the glasses doped with rare-earths performed with the EXAFS technique showed that the short-range order for Ga and Ge atoms in the glasses with $Ca_3Ga_2Ge_3O_{12}$ (garnet) and $Ca_3Ga_2Ge_4O_{14}$ (Ca-gallogermanate) compositions is similar to the order characteristic for the corresponding crystals [21], independent of the doping rare-earth ions.

2.2. Experimental methods and equipment

The optical absorption spectra were registered at the room temperature with the "Specord M-40" (Carl Zeiss Jena) spectrophotometer. The photoluminescence spectra were measured at the temperatures 300 and 85 K upon a frontal excitation and observation of the sample emission, using the equipment built at the Condensed Matter Spectroscopy Division (Institute of Experimental Physics, University of Gdańsk). The emission spectra were corrected for spectral sensitivity of the equipment. The Hanovia xenon lamp (P = 1000 W) was used as an excitation source. The wavelengths required for the excitation and observation were selected using the SPM-2 prismatic monochromator (Carl Zeiss Jena). Stepping motors driven by a computer and photomultipliers working in analogue or photon-counting regimes were used in the detection branch. The data from the latter were sent to the computer via a digital boxcar system. The Hamamatsu R 928 photomultiplier was used as a detector.

The luminescence decay times were measured and analysed, using the IBH 5000U fluorescence lifetime system. We used the excitation source 5000XeF and the detector TBX-04A. The investigated sample was mounted on the front-surface sample holder. In order to excite Ho^{3+} and Er^{3+}, the Spectra LED emitting at 455 and 372 nm was also used. In this case, the sample was oriented at the angle of 45° to the propagation direction of non-polarised incident light.

3. Results and discussion

3.1. Eu^{3+} luminescence centres

As noted in [17], none electron paramagnetic resonance (EPR) spectra in Eu-doped glasses of CaO-Ga$_2$O$_3$-GeO$_2$ system have been detected, thus meaning that the europium impurity is incorporated into the glass surroundings exclusively as Eu^{3+} (4f^6, ^{7}F$_0$) ions.

All the Eu-doped glass samples with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition are characterised by the optical absorption, emission and luminescence excitation spectra typical for Eu^{3+} ions (Fig. 1), which are caused by the forbidden *f-f*-transitions. The optical spectra observed in the 85 ÷ 300 K region are almost independent of the basic glass composition and

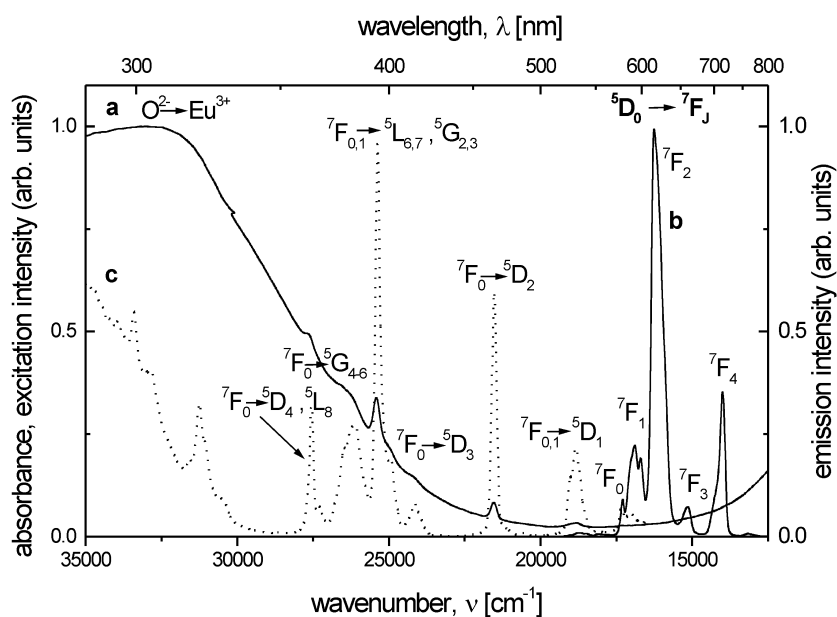**Fig. 1.** Optical absorption (a), emission (b) and luminescence excitation (c) spectra for Eu-doped glass with the Ca$_3$Ga$_2$Ge$_3$O$_{12}$ composition detected at 300 K.

temperature. In the luminescence excitation spectrum of Eu^{3+} ions, we observe a number of narrow bands that show a good correlation with the optical absorption bands (see Fig. 1, **a** and **c**). The intense broad absorption band with the maximum in the UV spectral range can be due to $O^{2-} \rightarrow Eu^{3+}$ charge-transfer band. The emission in the $570 \div 730$ nm region belongs to the $^5D_0 \rightarrow {}^7F_J$ (J = 1 $\div$ 4) transitions of Eu^{3+} ions (Fig. 1, **b**). Since the most intense emission line corresponds to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition, one can suppose that the Eu^{3+} luminescence centres in the $CaO-Ga_2O_3-GeO_2$ glass network occupy the sites lacking the inversion symmetry. The absence of emission from higher ^5D_J levels may be related to multiphonon or cross-relaxation processes, owing to a high concentration of Eu^{3+} centres in the glass.

The positions and relative intensities of Eu^{3+} spectral lines demonstrate a good agreement with the data for other Eu^{3+}-doped complex oxide crystals and glasses [1,2]. This also refers to the crystals activated with Eu^{3+} that manifest both the garnet and Ca-gallogermanate structures [22,23]. Particularly, the optical spectra of Eu^{3+} in the glasses of $CaO-Ga_2O_3-GeO_2$ system (Fig. 1) and the compositionally disordered Ca-gallogermanate crystal [22,23] are quite similar.

The luminescence decay curve for $^5D_0 \rightarrow {}^7F_2$ transition (λ_{max} = 615 nm) of Eu^{3+} centres in the $3CaO-Ga_2O_3-3GeO_2$-composition glass is obtained at the excitation wavelength λ_{exc} = 300 nm and the room temperature (see Fig. 2). We have tried to employ both the one- and two-exponential fittings of the decay curves. It has proved that the latter is much better than the former. Moreover, the three-exponential model shows no improvement to the fitting results. Thus, we conclude that the decay curve observed for Eu^{3+} luminescence centres can be well described in the framework of two-exponential approximation, with the lifetimes τ_1 = 0.90 and τ_2 = 1.55 ms.

3.2. Ho^{3+} luminescence centres

Ho impurity in the oxide compounds can manifest itself as Ho^{3+} ($4f^{10}$, $^5I_8$) or Ho^{2+} ($4f^{11}$, $^4I_{15/2}$) ions, with the characteristic optical and EPR spectra in each case. The X-band EPR spectra of Ho^{3+} and Ho^{2+} ions in the oxide crystals and glasses are observed at the liquid-helium temperatures [24]. In the glass with $3CaO-Ga_2O_3-3GeO_2$ composition doped with Ho, the EPR spectrum of Ho^{3+} is observed at the liquid-helium temperatures, too [18]. The EPR spectrum of Ho^{2+} ions is not detected even at T = 4.2 K, thus implying that the holmium impurity is incorporated into the $3CaO-Ga_2O_3-$
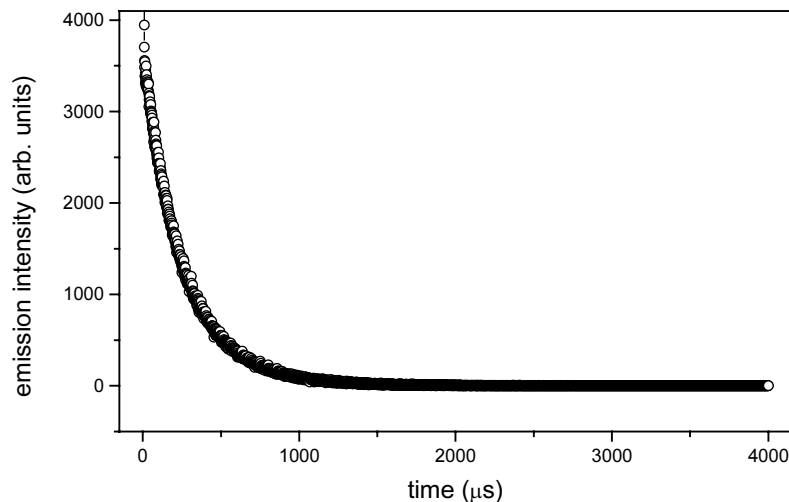

Fig. 2. Decay curve for Eu^{3+} luminescence centres ($^5D_0 \Rightarrow {}^7F_2$ transition, λ_{max} = 615 nm) detected at 295 K (open circles) and the results of the two-exponential fit (solid line, see text).

3GeO$_2$ glass network as Ho^{3+} ions.

The optical absorption spectrum of Ho-doped glass possessing 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition in the spectral range of 270 ÷ 700 nm (14000 ÷ 38000 cm^{-1}) consists of several absorption bands with a structure weakly resolved at the room temperature (see Fig. 3, **a**). One can notice that the undoped glasses of CaO-Ga$_2$O$_3$-GeO$_2$ system are transparent in the UV spectral range up to 280 ÷ 300 nm (Fig. 3, **b**) and are characterised by a high transparency in the IR range [16]. In accordance to [13,25], all the observed absorption lines (Fig. 3, **a**) are assigned to electronic *f-f*-transitions in Ho^{3+} ions, in general from the ground $^5I_8$ state to various excited states. The assignment of the multiplets is complicated, because the Stark components of the $^5I_8$ ground state are populated at the room temperature and many excited levels, each of them very close one to another, are involved in the absorption transitions. Moreover, inhomogeneous broadening of the optical bands of Ho^{3+}, associated with disordering of the glass structure, is revealed, too. As a consequence, most of the complex and weakly resolved bands observed by us can only be assigned to the groups of absorption transitions, as shown in Fig. 3, **a**.

A number of unresolved or weakly resolved bands (Fig. 3, **c**) are observed in the luminescence excitation spectra of Ho-doped glass with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition, which correlate well with the optical absorption transitions (see Fig. 3, **a**). The Ho^{3+} emission spectra in the visible (400 ÷ 800 nm) spectral range obtained both at the room and liquid-nitrogen temperatures are presented in Fig. 4. The emission spectra of Ho^{3+} ions excited at λ_{exc} = 448 nm consist of several bands, whose identification is given in Fig. 4. No better resolution of Ho^{3+} lines in the emission spectra could be achieved at the liquid-nitrogen temperatures (Fig. 4). This may evidence inhomogeneous broadening of the spectral lines.

The optical absorption and luminescence spectra of Ho^{3+} in the glasses of CaO-Ga$_2$O$_3$-GeO$_2$ system are almost independent of both the basic glass composition and the temperature in the 85 ÷ 300 K region and prove to be typical for the Ho-doped oxide glasses and crystals
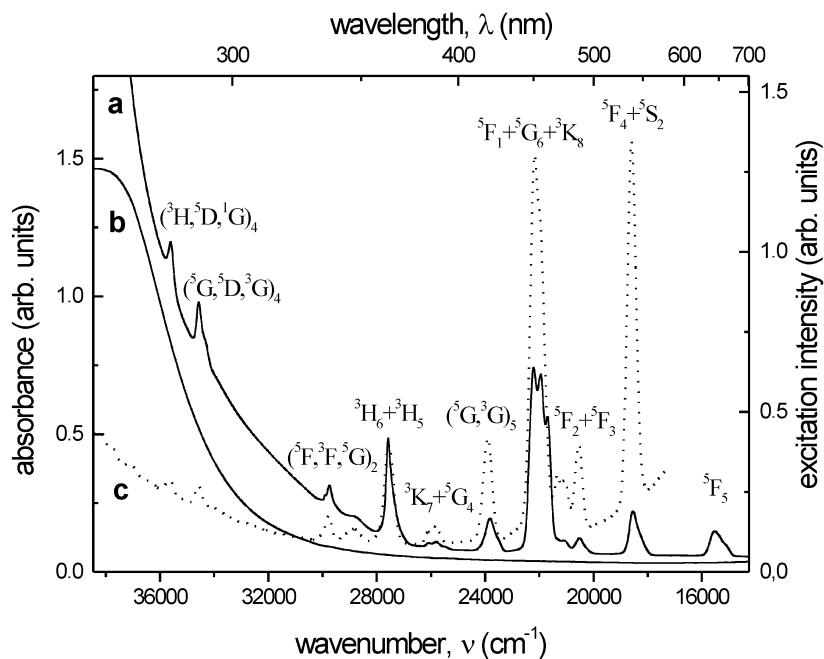

Fig. 3. Optical absorption (a, b) and luminescence excitation (λ_{obs} = 610 nm) (c) spectra of Ho-doped (a, c) and undoped (b) glasses with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition detected at 295 K.
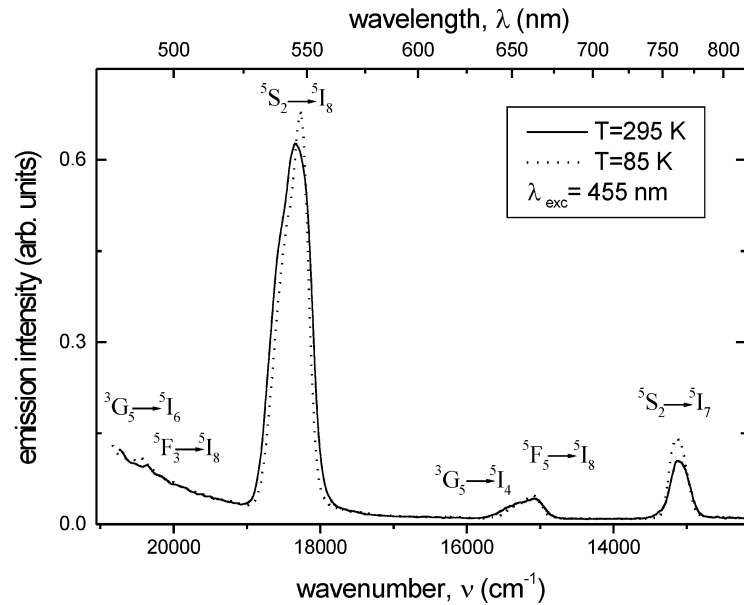
Fig. 4. Photoluminescence spectra of Ho-doped glass with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition excited with λ_{exc} = 448 nm and detected at 295 K and 85 K.
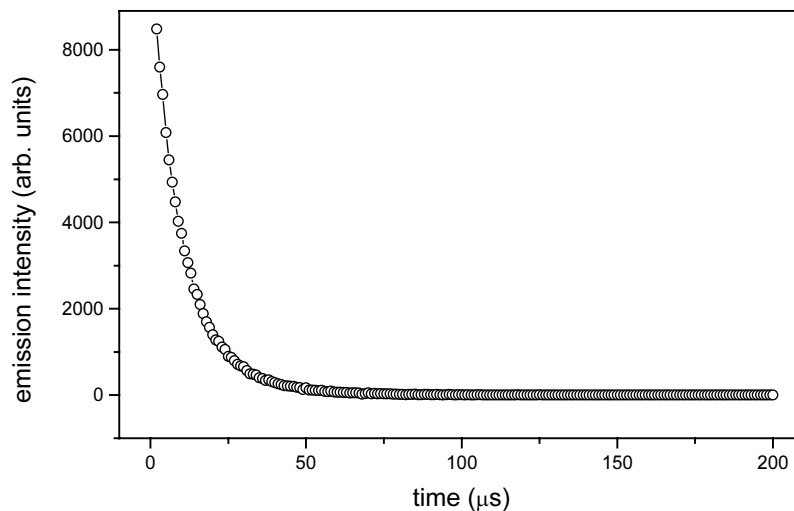
Fig. 5. Decay curve for Ho^{3+} luminescence centres ($^5S_2 \to {}^5I_8$ transition, λ_{max} = 545 nm) detected at 295 K (open circles) and the results of the two-exponential fit (solid line, see text).

[3,4,8,13]. One can note that, under the UV excitation, the intrinsic broad-band luminescence, which is characteristic for the undoped glasses of CaO-Ga$_2$O$_3$-GeO$_2$ system (see the results [26,27]), is not observed in the Ho-doped glasses.

The luminescence decay curve for $^5S_2 \to {}^5I_8$ transition (λ_{max} = 545 nm) of the Ho^{3+} centres in the glass with 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition is obtained at the excitation wavelength λ_{exc} = 455 nm and the room temperature (Fig. 5). The

observed decay curve can be described in framework of the two-exponential approximation, where the lifetimes are τ_1 = 3.9 and τ_2 = 7.5 µs. As in the case of Eu^{3+}, we suppose the two types of Ho^{3+} luminescence centres with different lifetimes, which correspond to different local environments in the glass structure.

3.3. Er^{3+} luminescence centres

Er impurity in the oxide compounds can

represent Er^{3+} and Er^{2+} ions, with different characteristic optical and EPR spectra. The X-band EPR spectra of Er^{3+} ions in the oxide crystals and glasses can be observed at low temperatures [24]. In the Er-doped glasses with 3CaO-Ga$_2$O$_3$-3GeO$_2$ compositions, only the EPR spectrum of Er^{3+} is observed at the liquid-helium temperatures [19]. Hence, the erbium is incorporated into 3CaO-Ga$_2$O$_3$-3GeO$_2$ glass surroundings as Er^{3+} (4f^{11}, ^{4}I$_{15/2}$) ions.

The optical absorption spectrum of Er-doped glass with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition detected in the 340 ÷ 800 nm (or 12000 ÷ 30000 cm^{-1}) region at room temperature includes a number of well-resolved characteristic absorption bands (Fig. 6, **a**). The linewidth and resolution of the observed absorption bands do not change at lowering temperature down to the liquid-nitrogen one. In accordance with the energy-level diagram and the literature data [9,25], all the observed absorption bands (see Fig. 6, **a**) are assigned to the electronic *f-f*-transitions of Er^{3+} ions from the ground ^{4}I$_{15/2}$ state to different excited states.

Seven bands clearly resolved at the room temperature (Fig. 6, b) are observed at 350 ÷

500 nm in the luminescence excitation spectrum of Er-doped glasses with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition. These bands strictly correspond to the optical absorption transitions (see Fig. 6, **a**). The emission spectra of Er^{3+} in the visible spectral range obtained under the excitation with λ_{exc} = 375 nm both at room and liquid-nitrogen temperatures consist of several lines that belong to the following transitions: ^{2}H$_{11/2}$ → ^{4}I$_{15/2}$, ^{4}S$_{3/2}$ → ^{4}I$_{15/2}$, ^{4}F$_{9/2}$ → ^{4}I$_{15/2}$ and ^{4}S$_{3/2}$ → ^{4}I$_{13/2}$ (Fig. 7). The optical absorption and luminescence spectra of Er^{3+} ions in the CaO-Ga$_2$O$_3$-GeO$_2$-system glasses are typical for the Er-doped oxide glasses [4,18,21,22]. Lowering of temperature to the liquid-nitrogen one leads to disappearance of the emission band corresponding to ^{2}H$_{11/2}$ → ^{4}I$_{15/2}$ transition (see Fig. 7). The linewidth of Er^{3+} bands in the absorption, emission and luminescence excitation spectra practically does not change, while the temperature lowers down to the liquid-nitrogen one (see Fig. 6 and 7). This is the evidence for inhomogeneous broadening of the spectral lines.

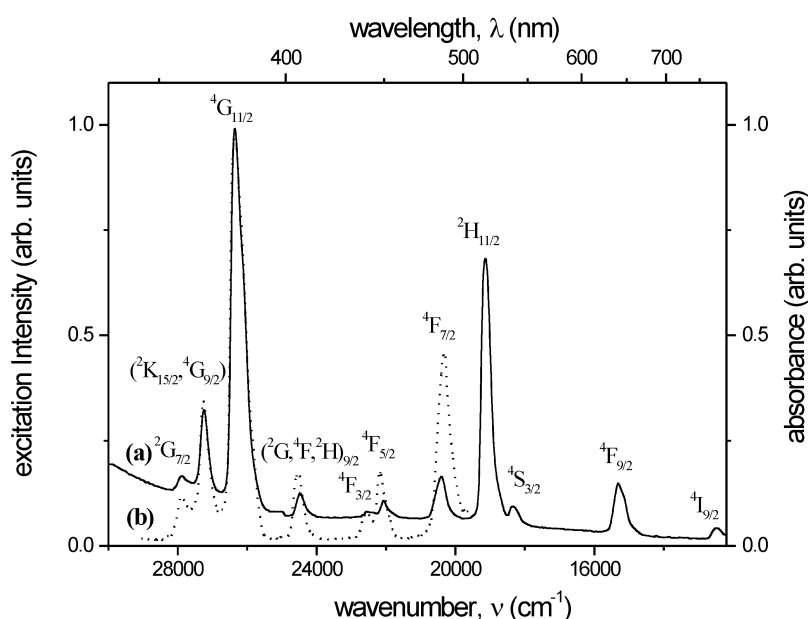The luminescence decay curve for ^{4}S$_{3/2}$ → ^{4}I$_{15/2}$ transition (λ_{em} = 555 nm) of Er^{3+} centres in

Fig. 6. Optical absorption (a) and luminescence excitation (λ_{obs} = 555 nm, ν_{obs} = 18328.34 cm^{-1}) (b) spectra of Er-doped glass with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition detected at 293 K.

the 3CaO-Ga$_2$O$_3$-3GeO$_2$-composition glass obtained at the excitation wavelength λ_{exc} = 375 nm and the room temperature is presented in Fig. 8. This curve can be described with the lifetimes τ_1 = 10.6 and τ_2 = 22.4 µs in frame of the two-exponential approximation. Similar results are obtained under the Spectra LED (372 nm) excitation of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition (λ_{em} = 545 nm). In this case the experimental decay curve for Er^{3+} centres is also described with the sum of two exponents, the appropriate lifetimes being equal to τ_1 = 10.7 and τ_2 = 25.0 µs.

3.4. Possible coordination and models of rare-earth luminescence centres in the CaO-Ga$_2$O$_3$-GeO$_2$ glass network

One can notice that the transition energies and relative intensity of the absorption lines for Eu^{3+}, Ho^{3+} and Er^{3+} ions in the glass with 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition are close to those measured for the other Eu-, Ho-and Er-doped crystals and glasses [1,2,4,5,7,28] and can be described on the basis of Judd-Ofelt theory [29,30]. Theoretical evaluation of the energies of absorption bands (E), the oscillator strength

(*f*), the Judd-Ofelt intensity parameters ($\Omega_{2,4,6}$) and the spectroscopic quality factor (Ω_4/Ω_6) shows a satisfactory agreement with the same parameters obtained experimentally from the Eu^{3+}, Ho^{3+} and Er^{3+} transitions in the glass with 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition.

Basing on the results obtained above and the literature data on the crystalline analogues, we can now consider a possible local structure and models for the rare-earth centres in the glasses of CaO-Ga$_2$O$_3$-GeO$_2$ system. In case of the ordered Eu-doped (the Eu content being 0.1 ÷ 3 at. %) calcium-gallium-germanium garnet crystal, the three types of Eu^{3+} luminescence centres are observed, whereas the only type of a so-called Eu^{3+} quasicentre is peculiar for the compositionally disordered Ca-gallogermanate crystals with the same Eu content [22,23]. The quasicentres of Eu^{3+} in the Ca-gallogermanate lattice are characterised by inhomogeneously broadened optical spectra, due to disordering of (1a) octahedral and (3f) tetrahedral sites [23]. The Eu^{3+} ions are incorporated into the lattice of compositionally disordered Ca-gallogermanate crystals in the (3e)-sites (the Thomson cube,
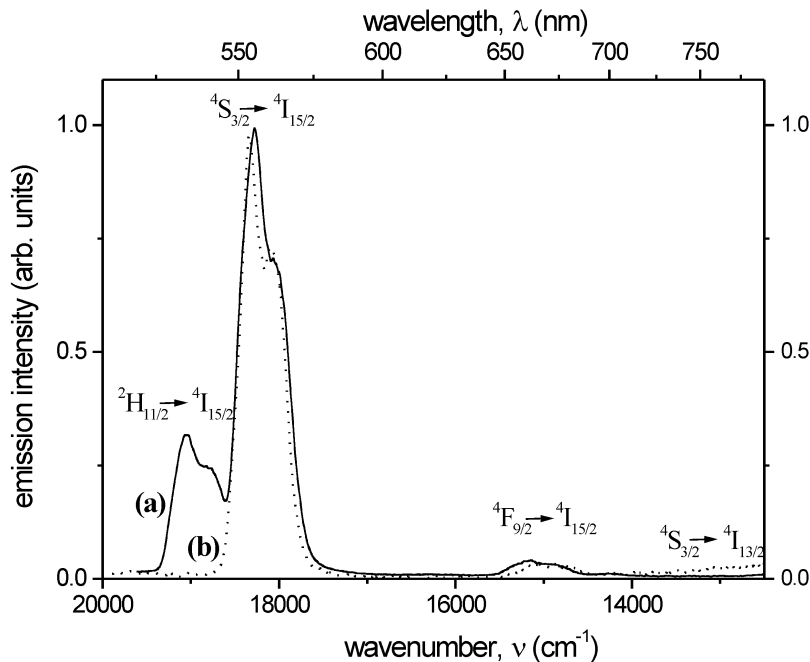
Fig. 7. Photoluminescence spectra of Er-doped glass with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition excited with λ_{exc} = 375 nm (ν_{exc} = 26323.16 cm^{-1}) and detected at 293 K (a) and 87 K (b).

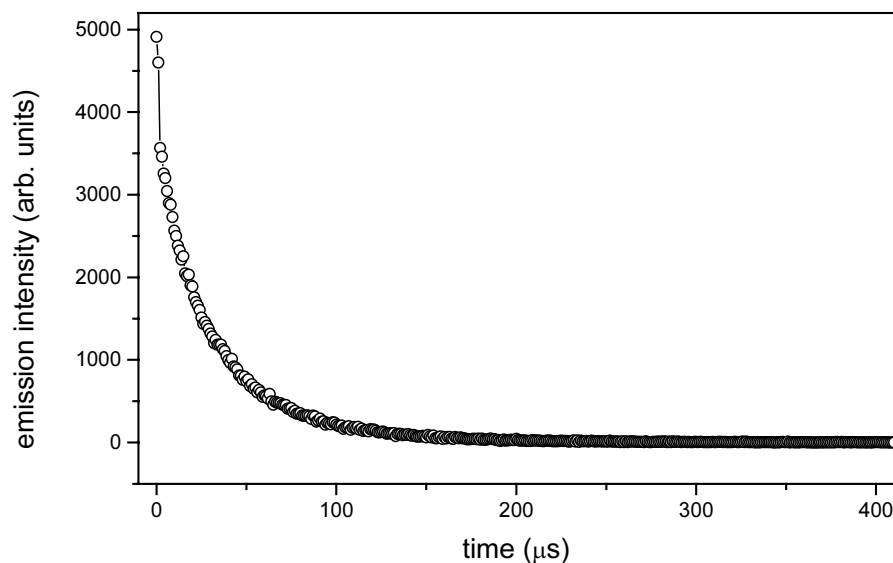**Fig. 8.** Decay curves for Er^{3+} luminescence centres ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition, λ_{max} = 555 nm) detected at 295 K (open circles) and the results of the two-exponential fit (solid line, see text).

eightfold coordination, local symmetry C_2). On the basis of similarity of the optical spectra of Eu^{3+} and the local structure of the glasses and the Ca-gallogermanate crystals, one can suppose that Eu^{3+} ions are incorporated into the sites with eightfold oxygen coordination in the CaO-Ga$_2$O$_3$-GeO$_2$ glass surroundings. Additional inhomogeneous broadening of Eu^{3+} spectral lines in the glass, when compare to disordered Ca-gallogermanate crystal, is caused by a continual disturbance of the short-range order.

Similar results have been also obtained for the Ho^{3+} and Er^{3+} luminescence centres. In particular, the best resolution for the absorption and luminescence spectral lines of Ho^{3+} is observed in Ca$_3$Sc$_2$Ge$_3$O$_{12}$ garnet crystals [13]. Significant inhomogeneous broadening of spectral lines of Ho^{3+} in 3CaO-Ga$_2$O$_3$-3GeO$_2$ glasses, in comparison with Ca$_3$Sc$_2$Ge$_3$O$_{12}$ crystals, is also related to a substitutional disorder and continual disturbance of the short-range order, which are characteristic for the glass structure. For the same reasons as for Eu^{3+} ions, we suppose that Ho^{3+} and Er^{3+} ions in the glass of CaO-Ga$_2$O$_3$-GeO$_2$ system are localised at the sites with eightfold coordination.

The analysis of the optical spectra for the glass of CaO-Ga$_2$O$_3$-GeO$_2$ system shows that we can consider an ensemble of Eu^{3+}, Ho^{3+}, Er^{3+} and other rare-earth centres, which are characterised with statistically distributed crystal field parameters caused by slightly different local environments.

The results for the luminescence kinetics testify clearly that the two types (or ensembles) of Eu^{3+}, Ho^{3+}, and Er^{3+} luminescence centres in the glass with CaO-Ga$_2$O$_3$-GeO$_2$ network exist in the sites with slightly different local environments and so different lifetime values. The lifetime analysis also corroborates availability of those two types of Cr^{3+} luminescence centres in the glass with 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition [31]. Confirmation of the coordination and local environment for the two different types of Eu^{3+}, Ho^{3+}, and Er^{3+} luminescence centres will be given elsewhere on the basis of analysis for L$_3$-edge EXAFS spectra in Eu-, Ho- and Er-doped glasses with the 3CaO-Ga$_2$O$_3$-3GeO$_2$ composition.

Conclusions

Basing on the optical spectra presented above

and the analysis of luminescence decay curves we can conclude the following:

1. The europium, holmium and erbium impurities are incorporated into $3CaO$-Ga_2O_3-$3GeO_2$ glass network as Eu^{3+} ($4f^8$, $^7F_0$), Ho^{3+} ($4f^{10}$, $^5I_8$) and Er^{3+} ($4f^{11}$, $^4I_{15/2}$) ions, respectively. The presence of Eu^{3+}, Ho^{3+} and Er^{3+} luminescence centres in the glasses of CaO-Ga_2O_3-GeO_2 system (with the amount of Eu, Ho and Er being about 0.7 wt %) leads to disappearing the broad-band "violet-blue" intrinsic luminescence, which is characteristic for the undoped glasses.

2. All the transitions of Eu^{3+}, Ho^{3+} and Er^{3+} ions observed in the optical spectra of Eu-, Ho- and Er-doped glasses with the $3CaO$-Ga_2O_3-$3GeO_2$ composition are identified. The optical absorption spectra of the rare-earth ions in the glasses under test are characterised by inhomogeneously broadened spectral lines caused by structural disordering of the glass structure. They can be analysed in framework of the Judd-Ofelt theory for the centres with statistically distributed crystal field parameters.

3. The emission of Eu-doped glass with the $3CaO$-Ga_2O_3-$3GeO_2$ composition observed in the region of 570 ÷ 730 nm refers to $^5D_0 \rightarrow {}^7F_J$ ($J = 1 \div 4$) transitions in Eu^{3+} ions. Under the excitation at 448 nm, the Ho-doped glass reveals the intense band with $\lambda_{max} = 545$ nm ($^5S_2 \rightarrow {}^5I_8$ transition) and several weak emission bands in the visible spectral range, which belong to the following Ho^{3+} transitions: $^5S_2 \rightarrow {}^5I_7$, $^5F_5 \rightarrow {}^5I_8$, $^3G_5 \rightarrow {}^5I_4$, $^5F_3 \rightarrow {}^5I_8$ and $^3G_5 \rightarrow {}^5I_6$. Under the excitation at 375 nm, the intense "green" ($^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions) and weak "red" emissions ($^4F_{9/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{13/2}$ transitions) are observed in Er-doped glasses. The Eu^{3+}, Ho^{3+} and Er^{3+} luminescence decay curves, measured at the room temperature, can be described well in frame of the two-exponential approximation, with the characteristic lifetimes for each rare-earth centres corresponding to the two sites with different local environments in the $3CaO$-Ga_2O_3-$3GeO_2$ glass surroundings. The EXAFS studies for the local environment for different Eu^{3+}, Ho^{3+} and Er^{3+} centres in the CaO-Ga_2O_3-GeO_2 glass network are in progress.

4. The results of optical studies presented by us confirm that the glasses of CaO-Ga_2O_3-GeO_2 system could be promising materials for the "red" phosphors, when activated with Eu^{3+}, the "green" lasers, as well as the IR LED-pumped up-converted lasers operating in the visible spectral range, when activated with Ho^{3+} and Er^{3+} ions.

Acknowledgements

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