The nature of intrinsic luminescence in glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system

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Abstract

Intrinsic luminescence of undoped glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system with different compositions is investigated. Using synchrotron excitation, the emission and time-resolved luminescence excitation spectra, as well as the luminescence kinetics are studied at $T = 8$ K for the undoped glasses and crystals with garnet $Ca_3Ga_2Ge_3O_{12}$ composition and the glasses with $Ca_3Ga_2O_6$ composition. The observed luminescence spectra strongly depend on the basic glass composition and the excitation energy. They consist of several (up to four) broad emission bands located in the visible spectral range. Basing on comparative analysis of the emission and excitation spectra and the decay kinetics in the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system, we propose recombination mechanism of the intrinsic luminescence. Specific models suggested for the intrinsic luminescence are supported by electron spin resonance spectroscopic results.

Keywords: germanate glasses, $Ca_3Ga_2Ge_3O_{12}$ garnet, intrinsic luminescence, synchrotron radiation, luminescence kinetics, recombination mechanism, radiation-induced defects, electron spin resonance (ESR)

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1. Introduction

Intrinsic luminescence is characteristic for a number of crystalline and vitreous (or glassy) compounds. It has numerous technical applications such as scintillators, phosphors, dosimetry, etc. The intrinsic luminescence is related to point defects and structural peculiarities of the host. Up to now, the nature of the intrinsic luminescence in complex (binary, ternary, etc.) silicate and germanate glasses has been studied insufficiently. The same also concerns the compounds of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system, which can be obtained in both crystalline and glassy states.

There exist three stable crystalline forms in the quaternary $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system: $Ca_3Ga_2Ge_3O_{12}$ (ordered garnet structure with the space group *Ia3d*) [1,2], $Ca_3Ga_2Ge_4O_{14}$ (substitutionally disordered Ca-gallogermanate structure, the space group *P321*) [2,3], $Ca_2Ga_2GeO_7$ (gelenite structure, the space group $P\bar{4}2_1m$) [2]. The corresponding glassy

forms have the composition similar to stoichiometric composition of the crystals [4]. Several crystalline compounds also exist in the ternary CaO-Ga_2O_3 system, in particular $Ca_2Ga_2O_6$ crystal [5]. Nominally pure glasses with $Ca_3Ga_2Ge_3O_{12}$, $Ca_3Ga_2Ge_4O_{14}$ and $Ca_2Ga_2O_6$ compositions of high optical quality and chemical purity have been obtained according to [4]. Large single crystals of the CaO-Ga_2O_3-GeO_2 system can be readily obtained with Czochralski technique [2,3]. It has been shown with X-ray scattering technique that the undoped glasses with $Ca_3Ga_2Ge_3O_{12}$, $Ca_3Ga_2Ge_4O_{14}$ and $Ca_2Ga_2O_6$ compositions are characterized by typical glassy-like structure factors and their glass network consists of gallium and germanium oxygen-coordinated tetrahedra and octahedra [6]. Detailed structural studies of the undoped glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions with EXAFS (Extended X-ray Absorption Fine Structure) technique have confirmed correlation between the local structures (short-range order arrangements) of the corresponding vitreous and crystalline compounds of CaO-Ga_2O_3-GeO_2 system [7].

Luminescence properties of the undoped glasses of CaO-Ga_2O_3-GeO_2 system have been reported for the first time in [8], where three different types of luminescence centres have been considered. In particular, emission bands with the maxima at 380 and 710 nm excited by pulsed nitrogen (N_2) laser (λ = 337.1 nm) distinctly reveal themselves at 80 K in the glasses with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2O_6$ compositions. According to [8], they can be related to two different centres of electron type, by analogy with the well-known F^+ and F centres in the crystals of simplest oxides [9]. The authors of [8] have also supposed that complex broad emission bands with the maxima located between 400 and 500 nm should be assigned to recombination luminescence of the ensemble of UV-induced transient O^- hole centres. The luminescence spectra of the glasses of CaO-Ga_2O_3-GeO_2 system have been studied in [10] at the room temperature under UV (Xe-lamp) excitation. Recombination nature of the broad emission bands with the maxima in the spectral region of 400–500 nm has been confirmed.

However, the nature and specific models of recombination luminescence centres in the undoped glasses and crystals of CaO-Ga_2O_3-GeO_2 system have not yet been clearly established. In this work we study the emission spectra, time-resolved luminescence excitation spectra and the luminescence kinetics for the glasses and crystals of CaO-Ga_2O_3-GeO_2 system under synchrotron excitation and at liquid-helium temperatures. On the basis of results obtained by us and the referenced data analysis, we reveal the nature and propose the recombination mechanism of the intrinsic luminescence in the glasses and crystals of CaO-Ga_2O_3-GeO_2 system.

2. Experimental details

All of undoped glasses of the CaO-Ga_2O_3-GeO_2 system were obtained in corundum crucibles with a standard high-temperature synthesis technique in accordance with [4]. Nominally pure $Ca_3Ga_2Ge_3O_{12}$ garnet crystals were obtained with Czochralski technique. Chemical composition of the samples obtained by us was controlled with X-ray

microanalysis technique, using a “Camebax” apparatus. A number of glass samples of high chemical purity and optical quality were selected for investigation, which had the compositions of $Ca_3Ga_2Ge_3O_{12}$ (calcium-gallium-germanium garnet), $Ca_3Ga_2Ge_4O_{14}$ (Ca-gallogermanate) and $Ca_3Ga_2O_6$. The samples used for spectroscopic measurements were cut to the approximate dimensions of $6\times4\times2$ mm^3 and polished.

The emission spectra, luminescence excitation spectra and the decay kinetics were studied at the Deutsches Elektronen Synchrotron (DESY, Hamburg), using the facility of SUPERLUMI station at HASYLAB described in [11]. All the measurements were carried out at $T = 8$ K. The emission spectra were measured in the range of 200–900 nm, using ARC “Spectra Pro 308” monochromator-spectrograph (the focal length 30 cm) in Czerny-Turner mounting equipped with Princeton Instruments CCD detector. Time-resolved luminescence excitation spectra were scanned with the resolution of 0.32 nm in the range of 3.8–10 eV with the aid of primary monochromator (the focal length 2 m) in 15° McPherson mounting, using HAMAMATSU R6358P detector with a secondary ARC monochromator. Integrated excitation spectra corresponded to the total signal formed by photomultiplier. The fast component of the spectra was registered just after the excitation pulse within the 0–5 ns time-gate, while the slow component – within the 100–180 ns one. Luminescence excitation spectra have been corrected for incident photon flux.

3. Results and discussion

3.1. Luminescence spectra under synchrotron excitation at low temperatures

In Fig. 1 we present the emission spectra for the glass with $Ca_3Ga_2Ge_3O_{12}$ composition, which are obtained at different energies of synchrotron excitation and the temperature of $T = 8$ K. The spectra are complicated and consist of at least four bands peaked near 500, 580, 700 and 780 nm, whose linewidths are close. Those bands are better perceptible (see Fig. 1, a) in case of the excitation with $E_{exc} = 4.43$ eV ($\lambda_{exc} = 280$ nm). Increase in the excitation energy leads to decreasing intensity of the long-wave bands and increasing intensity of the short-wave ones, together with a ‘blue’ shift of positions of the latter (Fig. 1, a and b). As a result, an intense band peaked near 450 nm and two weak bands located near 570 and 760 nm are observed in the luminescence spectrum (see Fig. 1, b), when the excitation is characterized by $E_{exc} = 5.46$ eV ($\lambda_{exc} = 227$ nm). The emission spectra obtained under synchrotron excitation (Fig. 1) are similar to those obtained under N_2-laser excitation [8] and the observed emission bands belong to luminescence centres of different types.

The time-resolved excitation spectra of the two short-wave emission bands peculiar for the glass with $Ca_3Ga_2Ge_3O_{12}$ composition are shown in Fig. 2. The excitation spectrum of the emission band, peaked near 450 nm (Fig. 1,b), consists of two well-resolved bands with the maxima close to 225 and 285 nm (Fig. 2, a), whereas the excitation spectrum of the emission band peaked near 570 nm (Fig. 1, b) consists of one band with the maximum at 255 nm (Fig. 2, b). Slow component dominates in the excitation spectrum of the emission bands peaked near 450 and 570 nm. It gives the main

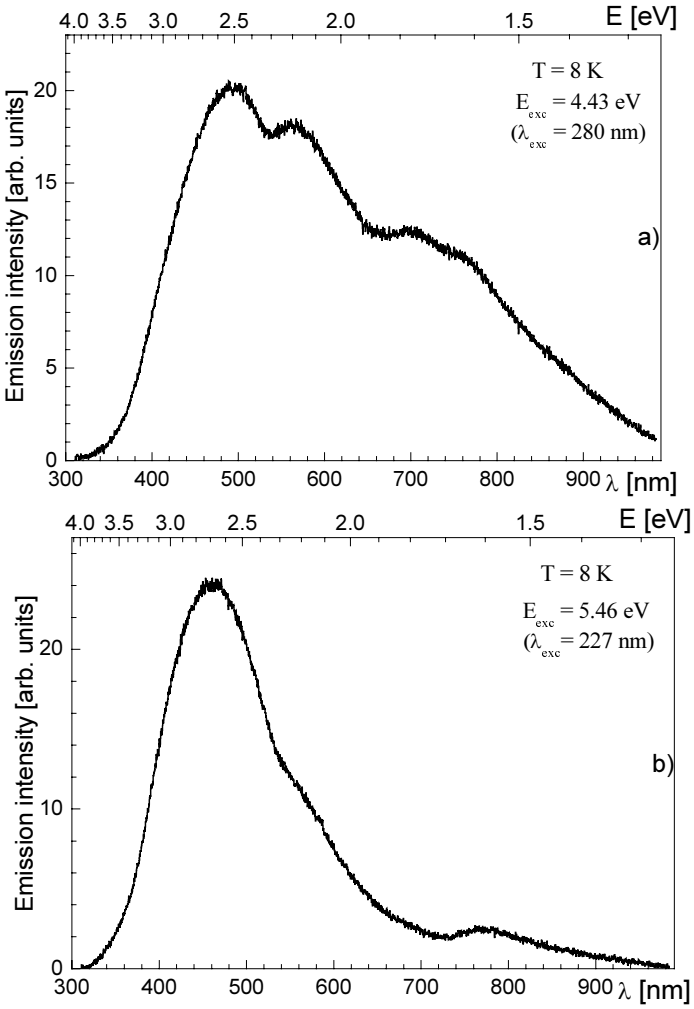

Fig. 1. Emission spectra detected at T = 8 K under synchrotron excitation with E_{exc} = 4.43 eV (a) and E_{exc} = 5.46 eV (b) for the glass with $Ca_3Ga_2Ge_3O_{12}$ composition.

contribution to the total spectrum (Fig. 2, a and b). The excitation spectra observed by us demonstrate also that the emission bands peaked near 450 and 570 nm (Fig. 1, b) belong to different types of luminescence centres. It should be noted that the long-wave emission bands peaked near 700 and 780 nm also belong to different luminescence centres, too.

For comparison with the spectra obtained for the glass with $Ca_3Ga_2Ge_3O_{12}$ composition (see Fig. 1 and 2), we have investigated and analyzed the luminescence spectra of the corresponding $Ca_3Ga_2Ge_3O_{12}$ garnet crystal. The emission and luminescence excitation spectra for the mentioned crystal are presented in Fig. 3 and 4, respectively. One can notice that the emission spectra of the garnet crystal are characterized by much narrower bands, when compare with the corresponding spectra for the garnet-composition glass (see Fig. 3).

The emission spectrum of $Ca_3Ga_2Ge_3O_{12}$ crystal for the case of excitation with E_{exc}=5.64 eV (λ_{exc}= 220 nm) consists of three broad bands with the maxima localized near 460, 560 and 700 nm (Fig. 3, b). As seen from Fig. 1, b, this spectrum in its short-wave region is similar to that of the glass, if detected at the excitation energy

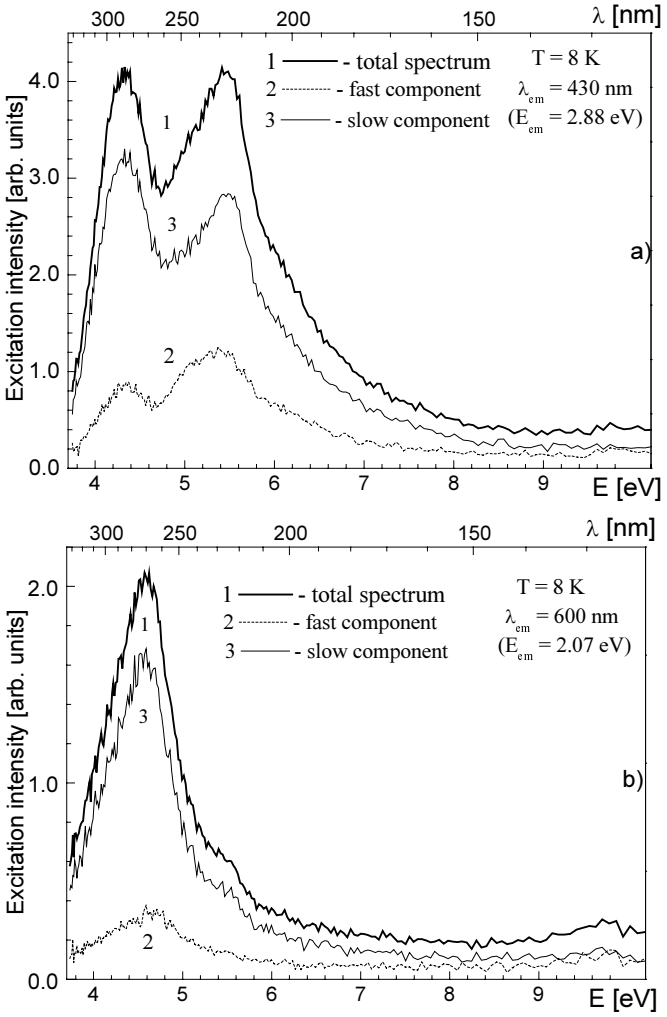

Fig. 2. Luminescence excitation spectra for the emission bands peaked near 450 nm (a) and 570 nm (b) in the glass with $Ca_3Ga_2Ge_3O_{12}$ composition (detected at T = 8 K).

E_{exc} = 5.46 eV (λ_{exc} = 227 nm). Increasing excitation wavelength leads to intensity redistribution and weak shift of the emission bands characteristic of the $Ca_3Ga_2Ge_3O_{12}$ crystal. In particular, two relatively narrow intense bands peaked at 450 and 700 nm and a broad band peaked near 670 nm (Fig. 3, b) are observed in case of the excitation energy E_{exc} = 3.90 eV (λ_{exc} = 318 nm).

In Fig. 4 we depict the time-resolved excitation spectra of the emission bands for $Ca_3Ga_2Ge_3O_{12}$ crystal, which are peaked near 460 and 560 nm.

The slow component dominates in all of the excitation spectra studied for the garnet crystal (Fig. 4). Basing on comparative analysis of the excitation spectra obtained for the glass and crystal with the same $Ca_3Ga_2Ge_3O_{12}$ composition, we can state that the bands peaked near 225 and 285 nm for the glass (Fig. 2) and those at 220 and 250 nm for the crystal (Fig. 4) belong to the excitation bands of emission with the maximum located close to 450 nm. The narrow band at 320 nm in the excitation spectrum of $Ca_3Ga_2Ge_3O_{12}$ crystal (Fig. 4, a) is not observed in the excitation spectra of the corresponding glass (Fig. 2) and may be referred to as an exciton band.

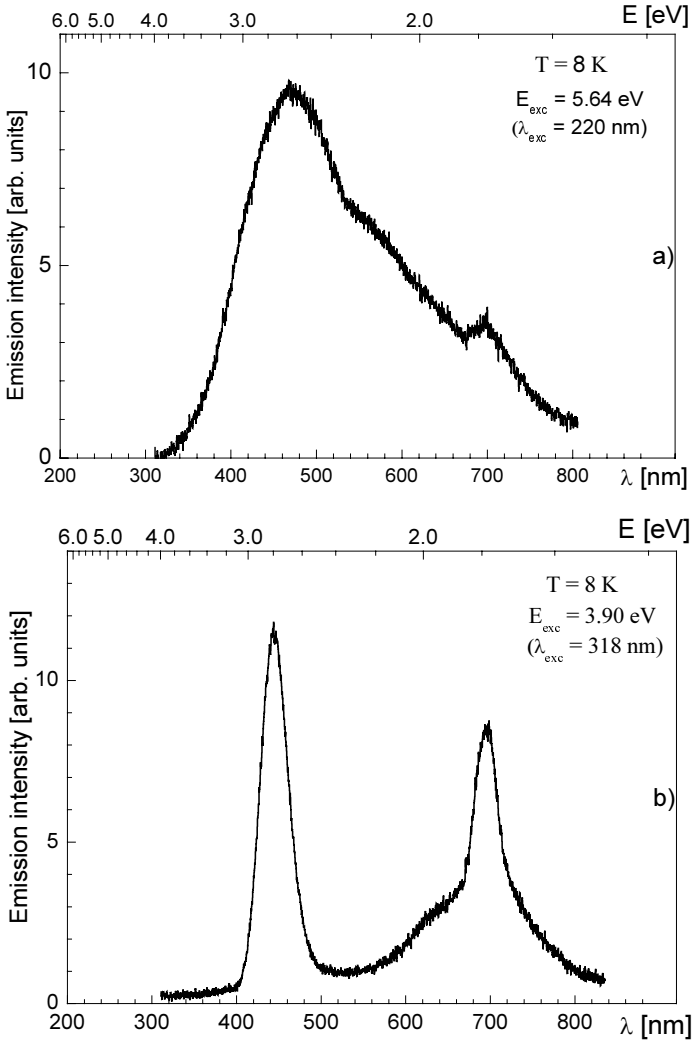

Fig. 3. Emission spectra detected at T = 8 K under synchrotron excitation with E_{exc} = 5.64 eV (a) and E_{exc} = 3.90 eV (b) for $Ca_3Ga_2Ge_3O_{12}$ garnet crystal.

The excitation spectra of the emission bands with the maxima at 560 nm (for the garnet crystal – see Fig. 3) and 570 nm (for the corresponding glass – see Fig. 1) include one band, which has a peak near 255 nm for the crystal (Fig. 4, b) and near 270 nm for the glass (Fig. 2, b). Thus, the emission bands located near 570 nm for the glass and 560 nm for the crystal with the composition $Ca_3Ga_2Ge_3O_{12}$ have similar excitation spectra and so could be assigned to the same luminescence centres or, at least, the centres with similar structures. It is worth noticing that the emission and luminescence excitation spectra for the germanate glass with $Ca_3Ga_2Ge_4O_{14}$ (Ca-gallogermanate) composition are very similar to the corresponding spectra for the glass with $Ca_3Ga_2Ge_3O_{12}$ composition. They have not been examined in the present study.

Instead, we have investigated synchrotron-excited luminescence spectra for the non-germanate glass with $Ca_3Ga_2O_6$ composition, in order to compare them to typical for the germanate glasses and crystals. The emission spectrum for the $Ca_3Ga_2O_6$-composition glass have been detected when the excitation energy is equal to E_{exc} = 4.88 eV

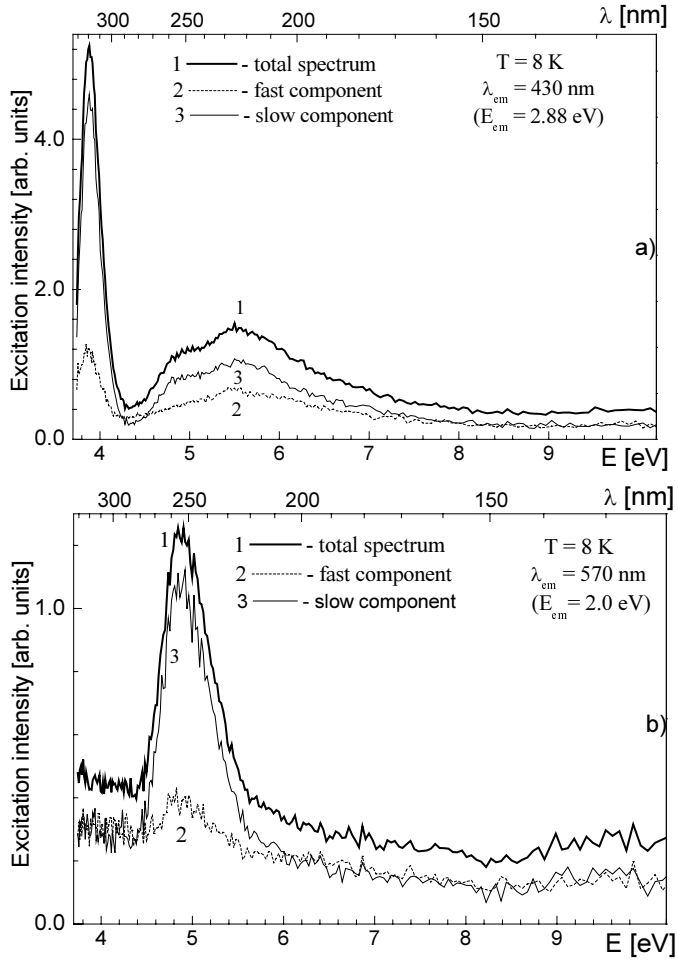

Fig. 4. Luminescence excitation spectra for the emission bands peaked near 460 nm (a) and 560 nm (b) in the $Ca_3Ga_2Ge_3O_{12}$ garnet crystal (detected at T = 8 K).

(λ_{exc} = 254 nm). It consists of two intense broad bands, with their maxima being close to 500 and 580 nm (see Fig. 5).

In the emission spectrum for the glass with $Ca_3Ga_2O_6$ composition, we have not observed two long-wave bands (Fig. 5), which are characteristic for the germanate glasses at similar excitation and temperature (Fig. 1). Thus, the long-wave bands in Ge-containing glasses should be related to Ge subsystem of the glass structure. At the same time, the positions of the emission bands located in the vicinity of 500 and 580 nm for the glass with $Ca_3Ga_2O_6$ composition (Fig. 5) practically coincide with the peak positions of short-wave bands for the glass with $Ca_3Ga_2Ge_3O_{12}$ composition, registered at close excitation energy and T = 8 K (see Fig. 1, a). This result clearly demonstrates that the emission bands near 500 and 580 nm for the glasses with both $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2O_6$ compositions belong to the same luminescence centres and could be therefore associated with oxygen or Ga subsystems of the glass network.

For the glass with $Ca_3Ga_2O_6$ composition, the excitation spectra of the emission bands with the maxima close to 500 and 580 nm are similar and consist, respectively, of an intense band with the peak located near 260 nm and a weak band peaked near 220 nm (see Fig. 6, a and b).

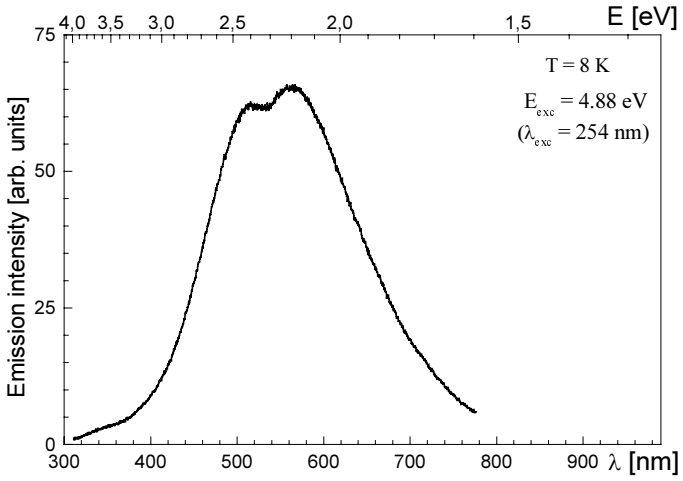

Fig. 5. Emission spectra detected at T = 8 K under synchrotron excitation with E_{exc}=4.88 eV for the glass with $Ca_3Ga_2O_6$ composition.

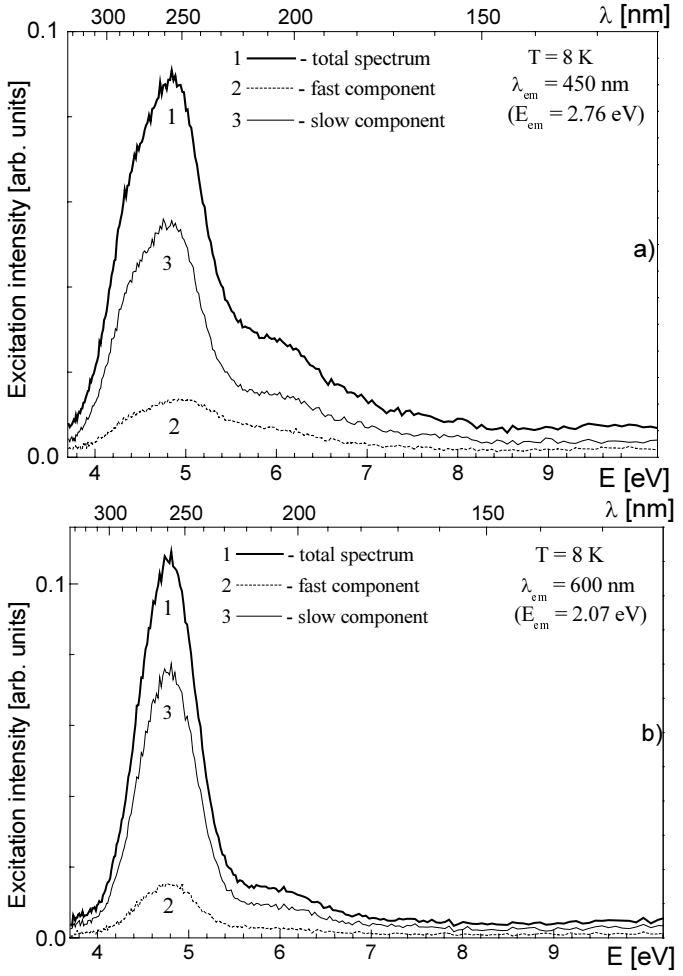

Fig. 6. Luminescence excitation spectra for the emission bands peaked near 500 nm (a) and 580 nm (b) in the glass with $Ca_3Ga_2O_6$ composition (detected at T = 8 K).

Quite similar excitation spectra for the both emission bands (near 500 and 580 nm) observed for the glass mentioned above (see Fig. 6, a and b) show that these bands belong to the same luminescence centres, with slightly different local environments in the glass network. Let us mark that the luminescence excitation spectra for the glass with the

composition $Ca_3Ga_2O_6$ (Fig. 6) differ from the excitation spectra of the corresponding emission bands detected for the glass with the garnet composition $Ca_3Ga_2Ge_3O_{12}$ (Fig. 2).

3.2. Luminescence kinetics

In order to determine the nature of intrinsic luminescence in the glasses and crystals of CaO-Ga_2O_3-GeO_2 system, we have studied decay kinetics of the emission. Fig. 7 depicts the decay curves for different emission bands detected for the glass with $Ca_3Ga_2Ge_3O_{12}$ composition under synchrotron excitation. The decay curves for the emission band at 430 nm may be satisfactorily described in the framework of simple two-exponential

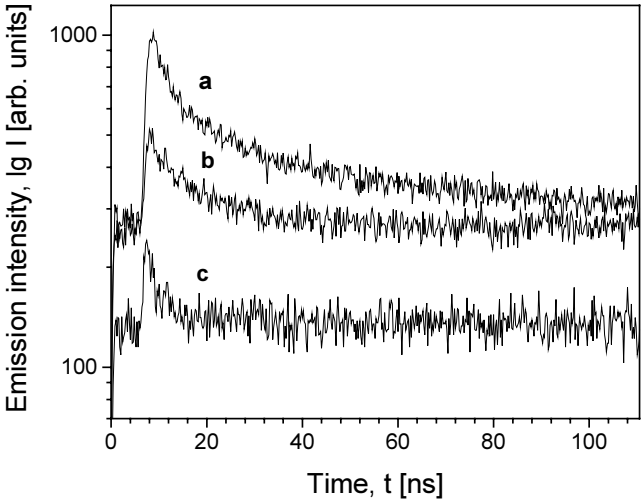

Fig. 7. Decay curves for the emission bands located near 430 nm (a, b) and 600 nm (c) in the glass with $Ca_3Ga_2Ge_3O_{12}$ composition, detected at T = 8 K under synchrotron excitation with λ_{exc} = 227 nm (a), λ_{exc} = 280 nm (b) and λ_{exc} = 267 nm (c).

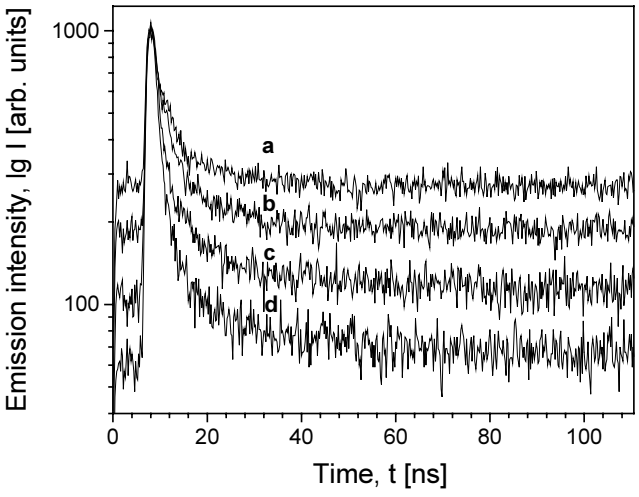

Fig. 8. Decay curves for the emission bands located near 600 nm (a, b) and 475 nm (c, d) in $Ca_3Ga_2Ge_3O_{12}$ crystal, detected at T = 8 K under synchrotron excitation with λ_{exc} = 255 nm (a), λ_{exc}= 245 nm (b, c) and λ_{exc} = 210 nm (d).

model, with the lifetimes τ_1 = 40.14 ns and τ_2 = 4.56 ns (at the excitation with λ_{exc} =227 nm – see Fig. 7, curve a) or τ_1 =10.52 ns and τ_2 =0.304 ns (at the excitation with λ_{exc} = 280 nm – see Fig. 7, curve b). The same two-exponential model yields the lifetimes τ_1 = 27.69 ns and τ_2 = 1.75 ns in case of the decay curve for the emission band with the maximum near 600 nm, obtained at the excitation energy λ_{exc} = 267 nm (Fig. 7, curve c).

Fig. 8 gives the decay curves for different emission bands detected for the crystal with $Ca_3Ga_2Ge_3O_{12}$ composition under synchrotron excitation. The curve for the emission band near 430 nm in that crystal can also be described in framework of the two-exponential model, where the lifetimes are τ_1 = 9.87 ns and τ_2 = 2.23 ns (for the excitation λ_{exc} = 255 nm – see Fig. 8, curve a) and τ_1 = 10.67 ns and τ_2 = 2.35 ns (for the excitation λ_{exc} = 245 nm – see Fig. 8, curve b). The emission band near 475 nm in the $Ca_3Ga_2Ge_3O_{12}$ garnet crystal is characterized by the decay curve with the lifetimes τ_1 = 13.15 ns and τ_2 =1.71 ns (for the excitation λ_{exc} = 245 nm – Fig. 8, curve c) and τ_1 = 19.59 ns and τ_2 = 1.62 ns (for the excitation λ_{exc} = 210 nm – Fig. 8, curve d).

Hence, the decay curves of the emission bands observed for both the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system are described by the lifetime values lying in the nanosecond range, which are characteristic of recombination mechanism of the intrinsic luminescence. Validity of the simple two-exponential model in description of the luminescence decays shows that the UV excitation and the corresponding synchrotron excitation lead to complex generation-recombination processes and creation of similar emission bands in the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system with the same chemical composition, particularly in the glass and crystal with the $Ca_3Ga_2Ge_3O_{12}$ composition. Following from the results presented above, one can see that the synchrotron excitation reveals recombination centres ascribed to the cation and anion subsystems of the glass and crystal structures.

In spite of our detailed luminescence spectra and decay kinetics investigations, we are not yet in a position to put forward specific models of the intrinsic luminescence in the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system. In order to analyze possible models of the intrinsic luminescence, we should involve the electron spin resonance (ESR) spectroscopic data on the electron and local structure of radiation paramagnetic centres, which are induced by ionizing (both UV and X-ray) radiation in the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system. This is done in the next subsection.

3.3. Mechanism of intrinsic luminescence in the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system

Owing to experimental luminescence spectra obtained under synchrotron, N_2-laser [9] and Xe-lamp [10] excitations, as well as the ESR spectroscopy of radiation-induced defects [12–16] in the undoped nominally pure glasses and crystals with $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2O_6$ compositions, we are now able to propose possible models and specific recombination mechanism of the intrinsic luminescence.

The ESR spectroscopy has shown [12–14] that the UV illumination gives rise to formation of electron E' (Ge) centres in the germanate glasses with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_3O_{12}$ compositions, which remain stable at the room temperature. The same UV illumination induces stable hole O^- centres, though exclusively in the non-germanate glasses with $Ca_3Ga_2O_6$ composition. The X- and γ– irradiation involves formation of the stable electron E′ (Ge) and hole O^- centres in the glasses with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_3O_{12}$ compositions and the hole O^- centres alone in the glass with $Ca_3Ga_2O_6$ composition. Let us stress that the intrinsic luminescence in all of Ge-containing glasses of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system has not been observed under the X-ray excitation.

The electron E' (Ge) and the hole O^- centres in the glass network are characterized by high thermal stability and their ESR spectra are still observed at so high temperatures as 550 K [12–14]. The optical absorption band of the electron E' (Ge) centres in the glass with $Ca_3Ga_2Ge_3O_{12}$ composition has not been revealed, because this band is situated near the edge of fundamental absorption ($\lambda < 300$ nm), whereas the hole O^- centres manifest a broad optical absorption band in the spectral region of 350–500 nm, with a pronounced maximum near 430 nm [10,12].

It has been shown in [10] that prolonged continues UV irradiation of the glasses of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system practically does not modify the intensities and positions of the intrinsic luminescence bands. The intrinsic luminescence cannot be regarded as a result of either electron E′ (Ge) centres or Ge-related oxygen deficient centres (GODCs) [17,18], because it is also observed in the non-germanate glasses with $Ca_3Ga_2O_6$ composition. At the same time, the emission bands observed in Ge-containing glasses could be assigned to fast recombination of the ensemble of transient O^- hole centres, induced by UV and synchrotron radiation. The proposed recombination mechanism is supported by the ESR spectroscopy, which certifies absence of any stable UV-induced O^- hole centres in the Ge-containing glasses with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_3O_{12}$ compositions [12–14]. On the basis of these results, we may describe the recombination mechanism of the intrinsic luminescence for Ge subsystem of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glass structure by the following relation:

$$(\text{-O = Ge-O-Ge = O-}) + h\nu_{exc} \Rightarrow E'(Ge)_{stab} + O^- + e \Rightarrow E'(Ge)_{stab} + h\nu_{em} . \qquad (1)$$

A presence of more that one band in the intrinsic luminescence spectrum might be explained by existence of several types of O^{2-} anions in the sites of non-bridging oxygen, which coordinate different cations in the glass network.

For the same reasons, it has been concluded that the intrinsic luminescence of the garnet crystal $Ca_3Ga_2Ge_3O_{12}$ under synchrotron (Fig. 3) and the corresponding UV excitations could be related to recombination of transient O^- hole centres. This result correlates with the ESR spectroscopic data, because the ESR spectra of the O^- hole centres have not been observed in the UV-irradiated $Ca_3Ga_2Ge_3O_{12}$ garnet crystal [15].

The other emission bands observed in the glasses with all basic compositions should be ascribed to recombination of transient electron centres, induced by the UV and

corresponding synchrotron radiation. The most probable unstable electron centres in the glasses of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system can be E′ (Ga) centres [19,20], since their ESR spectra have not been observed in all the samples under investigation. In this case, the recombination mechanism of the intrinsic luminescence in the glass with $Ca_3Ga_2O_6$ composition under UV excitation may be presented as

$$(\text{- O= Ga - O - Ga=O-}) + h\nu_{exc} \Rightarrow E'(Ga) + e + O^-_{stab} \Rightarrow h\nu'_{em} + O^-_{stab}\ . \qquad (2)$$

For the Ga subsystem in the glasses with $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_3O_{12}$ compositions, we describe the recombination mechanism of the intrinsic luminescence under UV excitation using the following relation:

$$(\text{ - O = Ga - O - Ga = O - }) + h\nu_{exc} \Rightarrow E'(Ga) + e + O^- + e \Rightarrow h\nu''_{em} + O^{2-}\ . \qquad (3)$$

Significant bandwidths of the intrinsic luminescence are caused by presence of several types (ensembles) of recombination O^- and E' (Ga) centres, with slightly different local environments in the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glass network. This is confirmed by the luminescence kinetics presented above and the ESR studies [12–14]. As a conclusion, the proposed models for the recombination intrinsic luminescence involving Eqs. (1)–(3) are in good agreement with the ESR spectroscopy.

4. Conclusions

The analysis of the experimental results obtained in the present work and the literature data has comprised the following:

- Under UV and synchrotron excitations, intense intrinsic luminescence with complex broad bands has been observed in the visible spectral region for all of the undoped glasses and crystals of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system.
- The spectral positions and the structure of the observed emission bands depend essentially on both the excitation energy and basic composition of the glasses or crystals.
- Decay curves of the emission bands for the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system are fairly described in framework of the two-exponential model, with the lifetimes lying in the nanosecond range, which is typical for recombination mechanisms of the intrinsic luminescence.
- The emission bands observed in the Ge-contained glasses are associated with fast recombination of the ensemble of transient O^- hole centres. The latter are induced by the UV radiation and the corresponding synchrotron radiation and are localized at different sites of non-bridging oxygen in the glass network.
- The emission bands observed in all of the glasses and crystals of $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system could be related to recombination of transient E′ (Ga) electron centres, induced by the UV and synchrotron radiation at the structural sites with different local environments.

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