

# INTRINSIC LUMINESCENCE OF THE UNDOPED GLASSES OF (CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub>) SYSTEM\*

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For the first time the intrinsic luminescence in the undoped (CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub>) glasses with different composition has been found and investigated in the 80 ÷ 300 K temperature range. The new glasses of high chemical purity and optical quality with stoichiometric composition similar to that in calcium-gallium-germanium garnet (Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>), trigonal Ca-gallogermanate (Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub>), and Ca<sub>3</sub>Ga<sub>2</sub>O<sub>6</sub> crystals were obtained by the high-temperature synthesis method. The luminescence and photoexcitation spectra analysis, supported by EPR spectroscopy data, yields the following results: (i) the UV-excited non-elementary broad emission band with maxima at roughly 500 nm and 420 nm in the (CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub>) glasses is due to recombination of ensemble of the transient hole O<sup>-</sup> centres; (ii) the emission bands with maxima at nearly 380 and 710 nm, which were distinctly revealed in glasses with the Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub> and Ca<sub>3</sub>Ga<sub>2</sub>O<sub>6</sub> compositions, are assigned to the luminescence of UV-induced electron centres of two different types. Possible models of the luminescence centres in (CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub>) glass network are discussed.

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## 1. Introduction

The studies of nature and mechanisms of the photo- and thermally-stimulated luminescence of intrinsic and radiation-induced centres in the complex oxide compounds with disordered structure (compositionally (or substitutionally) disordered crystals, glasses, ceramics, etc.) are the current topics of solid state physics and modern technology of the materials for tunable solid state lasers and luminescent materials for detectors and transformers of ionizing radiation. The optical and EPR spectroscopies provide the powerful techniques for these investigations. The suitable objects for such studies are compounds which can be obtained in both the crystalline and vitreous (or glassy) states.

The compounds of (CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub>) threefold system have been selected for our studies. In this system three stable crystalline compounds: Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>

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(structure of garnet, space group —  $Ia3d$ ),  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (structure of Ca-gallogermanate, space group —  $P321$ ), and  $\text{Ca}_2\text{Ga}_2\text{GeO}_7$  (structure of gelenite, space group —  $P42_1m$ ) exist [1, 2]. The optical absorption, luminescence and EPR spectra of the intrinsic and radiation-induced centres in the lattice of crystalline compounds of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  system, particularly in the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  ordered crystals and  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  compositionally disordered crystals are published earlier in Refs. [3–10]. These results will be applied for comparison with the spectroscopic properties of glasses with the same compositions.

The possibility to obtain the compounds of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  system in glassy state and their possible applications has been originally reported in Refs. [11–13]. We have obtained the  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses of a high chemical purity and optical quality with different stoichiometric compositions both undoped and doped with transition metals' (Cr, Mn, Nd, Eu, Ce, etc.) ions. The optical and luminescence properties of the Cr-doped glasses with the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  stoichiometric composition are published in Ref. [14]. The X-band EPR spectra of  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{3+}$  impurity ions in glasses of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  system with different compositions were investigated in Ref. [15]. During structural investigation with the X-ray diffraction technique it was shown that the obtained compounds of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  system have a real glass structure without any traces of crystalline phases. Comparative analysis of the X-ray diffraction data for glasses with different compositions and their well-known crystalline analogies (garnet, Ca-gallogermanate and gelenite) proves that the glass network consists of gallium and germanium oxygen coordinated octahedra and tetrahedra [16]. Detailed investigations of the complex structure of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses are in the progress and will be published in a separate paper.

Previous studies of the intrinsic photoluminescence and thermally-stimulated luminescence in  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses were presented in Ref. [17]. This paper reports new experimental results and the possible models of luminescence centres in the undoped glasses of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  system.

## 2. Experimental procedure

The undoped glasses of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  system of high chemical purity and optical quality with different stoichiometric compositions were obtained in the corundum crucibles by the standard high-temperature synthesis using a KO-4 electrical furnace [13]. The chemical composition of the obtained glasses was controlled by the X-ray microanalysis technique using a "Camebax" apparatus. The presence of the impurity paramagnetic ions and radiation-induced paramagnetic centres in glasses was controlled by the EPR technique. For investigations the glasses of stoichiometric compositions similar to that in calcium-gallium-germanium garnet ( $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  or vitreous CGGG), trigonal Ca-gallogermanate ( $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  or vitreous Ca-gallogermanate), and  $\text{Ca}_3\text{Ga}_2\text{O}_6$  crystals were selected. Samples for optical measurements were cut and polished to the approximate size of  $10 \times 6 \times 3 \text{ mm}^3$  and for EPR measurements were cut to the approximate size of  $8 \times 4 \times 2 \text{ mm}^3$ .

Laser excitation luminescence was performed by a pulsed LGI-21 nitrogen laser at  $\lambda_{\text{exc}} = 337.1 \text{ nm}$ . The emission was analyzed with an SF-4A monochroma-

tor and detected with an FEU-51 photomultiplier. The photoexcitation of samples was carried out using an DKSEL-1000 lamp (250 ÷ 600 nm spectral region) with an 3MR-3 monochromator. Optical absorption spectra of the UV-irradiated glasses were registered at room temperature using a "Specord M-40" commercial spectrophotometer.

The X-band EPR measurements were carried out using an RE-1306 and RADIOPAN SE/X-2544 commercial rf spectrometers, operating in the high-frequency (100 kHz) modulation mode of magnetic field in the 77 ÷ 300 K temperature range. The  $g_{\text{eff}}$  parameters of paramagnetic centres in each case were defined from the experimental spectra through resonance relationship. The microwave frequency was determined by means of DPPH frequency marker ( $g = 2.0036 \pm 0.0002$ ).

### 3. Experimental results and discussion

Figure 1 shows the luminescence spectra of the undoped ( $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ ) glasses with different compositions, excited by the  $\text{N}_2$ -laser ( $\lambda = 337.1$  nm). The observed spectra (Fig. 1, curves 1'-3') consist of broad non-elementary band with maxima at nearly 490 nm (for vitreous CGGG), 500 nm (for glasses with  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition), 420 and 500 nm (for vitreous Ca-gallogermanate) at room temperature. The better resolution of the complex luminescence bands in all the investigated glasses was observed at liquid nitrogen temperatures (Fig. 1, curves 1-3). The relative increasing of emission intensity only in the 710 nm region (Fig. 1, curve 2) was observed in vitreous CGGG at 80 K, whereas in the glasses with  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition distinctly revealed the intense emission band with a maximum at 710 nm (Fig. 1, curve 1). The weak emission band with a maximum at about 390 nm was observed also in the glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition at 295 and 80 K. The luminescence spectrum of vitreous Ca-gallogermanate at 80 K consists of weakly-resolved band with a maximum at about 380 nm, the intense broad bands with maxima at 420 and 500 nm, and the weak band with a maximum at about 710 nm (Fig. 1, curve 3). The complex luminescence spectra in glasses with different compositions consist of the same emission bands with weakly-shifted maxima (Fig. 1). The intensity and resolution of emission bands depend on glasses' compositions. The three emission bands were revealed most distinctly in glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition. Therefore, we suggest that in ( $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ ) glasses at least three types of luminescence centres exist.

Figure 2 shows the temperature dependence of emission bands intensity in glasses with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  and  $\text{Ca}_3\text{Ga}_2\text{O}_6$  compositions in the 85 ÷ 300 K range. The analysis of these temperature dependences has shown that the band with a maximum at 490 nm (2.48 eV) in glasses with the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  composition is characterized by two values (0.02 eV and 0.05 eV) of the activation energy. In glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition the emission bands with maxima at near 500 and 710 nm (2.48 and 1.72 eV) are characterized by 0.04 eV and 0.06 eV values of activation energy, respectively, whereas the intense band with a maximum at 390 nm (3.18 eV) has a complicated temperature dependence with two values (0.18 eV and 0.04 eV) of activation energy. The intensity of emission band with a maximum at 380 nm, which was observed in the vitreous Ca-gallogermanate, is weakly dependent on temperature. Complex temperature dependences of emission

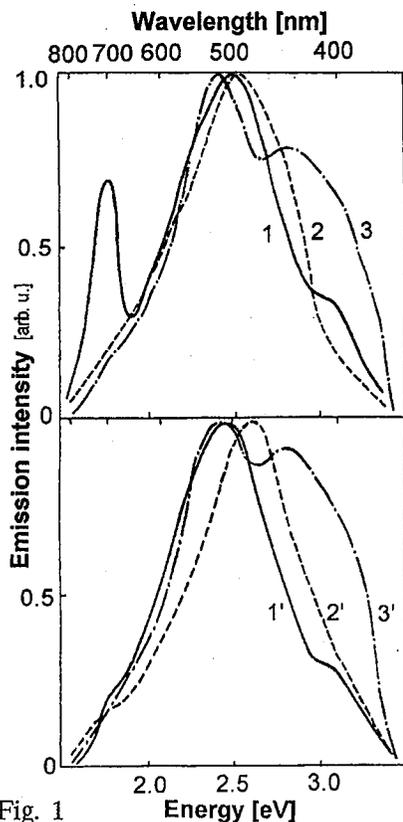


Fig. 1

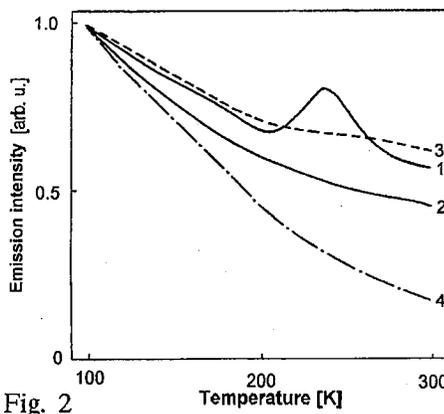


Fig. 2

Fig. 1. The luminescence spectra of undoped  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  (1, 1'),  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  (2, 2'), and  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (3, 3') compositions excited by  $\text{N}_2$ -laser and registered at 80 K (1-3) and 295 K (1'-3').

Fig. 2. Temperature dependence of the emission bands intensity with the maximum at about 2.48 eV (1) for glasses with the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  composition and the maxima at about 2.48 eV (2), 3.18 eV (3), and 1.72 eV (4) for glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition.

bands intensity evidence that the most probable mechanisms of intrinsic luminescence in the  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses may be related to the processes of generation-recombination and mutual transformation of electron and hole trapped centres at UV-excitation.

The photoexcitation spectra of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses with different compositions (Fig. 3) consist of broad non-elementary band with maxima at about 280 nm (for glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition), 275 nm (for glasses with the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  composition), and 265 nm (for glasses with the  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  composition) at room temperature. The asymmetric shoulders at nearly 320 and 240 nm were observed in photoexcitation spectra of glasses with  $\text{Ca}_3\text{Ga}_2\text{O}_6$  and  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  compositions, respectively, whereas the photoexcitation spectrum of vitreous CGGG consists of approximately symmetric broad band. Thus the pho-

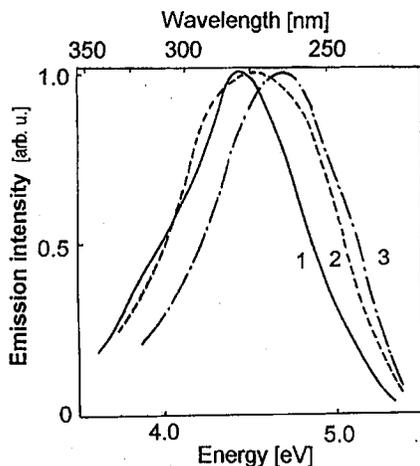


Fig. 3. The photoexcitation spectra of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  (1),  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  (2), and  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (3) compositions, registered at 295 K.

toexcitation spectra (Fig. 3) also indicate the presence of several types of luminescence centres, which are characterized by the complex nature of recombination processes in the  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glass network.

The analysis of the luminescence and photoexcitation spectra in the glasses with different compositions and their temperature dependences (Figs. 1-3) shows that the observed complex spectra belong to at least three different types of luminescence centres, which are characterized by emission bands with maxima at about 380-390 nm (I type), 490-500 nm and 420 nm (II type), and 710 nm (III type). These centres may be related to non-controlled impurities or intrinsic defects of glass network. The  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses are characterized by a high chemical purity and optical quality [13, 14], but for all activated and non-activated glasses the iron impurity is characteristic [15]. Isotropic EPR signals at  $g_{\text{eff}} = 4.29$  and  $g_{\text{eff}} = 2.00$ , which are observed in  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses, were assigned to isolated  $\text{Fe}^{3+}$  ( $3d^5$ ,  ${}^6S_{5/2}$ ) ions in the octahedral and tetrahedral sites with a strong rhombic distortion and in the octahedral sites with nearly cubic symmetry, respectively [15]. The total concentration of  $\text{Fe}^{3+}$  ions in the best samples of undoped glasses was approximately 10 times less than the one in the samples doped with transition metals' ions and does not exceed  $10^{-3}$  wt.%. Investigation of samples with different iron concentrations showed that the intensity of intrinsic luminescence is independent of  $\text{Fe}^{3+}$  concentration. Consequently, the observed luminescence spectra in the  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses are not related with the iron and other non-controlled impurities and may be connected with different intrinsic defects of glass network.

It is generally acknowledged that the main intrinsic defects in the oxide crystals and glasses are the anion, i.e., oxygen and different cation vacancies. Several types of the lattice  $\text{O}^{2-}$  anions with different local symmetries exist in the complex oxides such as  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  compounds. The  $\text{O}^{2-}$  anions occupy the

general h-sites ( $C_1$  local symmetry) only in the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  crystals, whereas in the Ca-gallogermanate disordered crystals three types of anion sites with the  $C_1$  ( $6g_1$ - and  $6g_2$ -sites) and  $C_3$  ( $2d$ -sites) local symmetries exist [1, 2, 10]. The structure of Ca-gallogermanate crystals is characterized by the statistical occupancy of the octahedral  $1a$ - and tetrahedral  $3f$ -sites by  $\text{Ga}^{3+}$  and  $\text{Ge}^{4+}$  cations [2]. The  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glass structure is the most similar to the structure of compositionally-disordered Ca-gallogermanate crystal. But the glass structure is characterized by both the statistical distribution of the  $\text{Ga}^{3+}$  and  $\text{Ge}^{4+}$  cations on octahedral and tetrahedral sites and the continual disturbance of a short-range order, which destroys a long-range order. Therefore, at least three types of the  $\text{O}^{2-}$  anions coordinate three different cations' sites in the  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glass network. It should be distinguished the bridging and non-bridging oxygen in a glass structure. In general, the real glass network may contain three types of non-bridging oxygen and three types of cation vacancies. As it was shown in Refs. [8-10] the most probable intrinsic defects in  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  crystals are the oxygen and  $\text{Ge}^{4+}$  vacancies, because  $\text{GeO}_2$  is the most volatile component of the melt. Concentrations of the oxygen and germanium vacancies in glasses are much larger than that in crystals with the same chemical composition, which is connected with synthesis peculiarities of crystals and glasses [1, 2, 13].

The oxygen and germanium vacancies are the effective traps for radiation-generated electrons and holes, respectively. As it was shown by EPR technique the UV-irradiation of Ge-containing glasses at 300 K leads to the formation of the stable electron centres generally (Fig. 4a, b, centres of the I type). Efficiency of generation of the electron centres decreases with a decrease in  $\text{GeO}_2$  content in glass composition and in the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  glasses the centres of the I type were not observed (Fig. 4c). The stable hole centres of the II type were only observed in the UV-irradiated glasses with the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  composition. The electron centres are characterized by approximately axially symmetric  $g$ -tensor and were interpreted as electrons, trapped at the sites of oxygen vacancies in the dangling  $sp^3$  hybrid orbitals of germanium ions, i.e., germanium  $E'$  or  $E'(Ge)$  centres [18-20]. Optical absorption bands of the  $E'(Ge)$  centres were not observed. Perhaps these bands are weak and localized near the edge of the fundamental absorption ( $< 300$  nm). The X-irradiation of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses leads to the formation of stable centres of two types: the I — electron  $E'(Ge)$  centres and the II — hole trapped centres. The EPR spectrum of X-induced hole centres is similar to the spectrum of UV-induced hole centres of the II type (Fig. 4c) and is characterized by statistical distributions of  $g$ -values. The centres of the II type are interpreted as an ensemble of the  $\text{O}^-$  centres, i.e., holes, trapped on non-bridging oxygen in different sites of glass network [19, 20]. Optical absorption of stable  $\text{O}^-$  centres in the  $\text{Ca}_3\text{Ga}_2\text{O}_6$  glasses consists of inhomogeneously broadened band with a maximum near 400 nm. It should be noted that the intrinsic luminescence of  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses under X-ray excitation was not observed at 80 and 300 K.

Let us consider briefly some referenced data on the nature and mechanisms of intrinsic luminescence in the typical oxide crystals and glasses. The emission bands of the  $\text{F}^+$  and  $\text{F}$  centres were observed at 300 K in additively coloured alkaline earth ( $\text{CaO}$ ,  $\text{MgO}$ , etc.) single crystals [21] and polycrystalline powders [22].

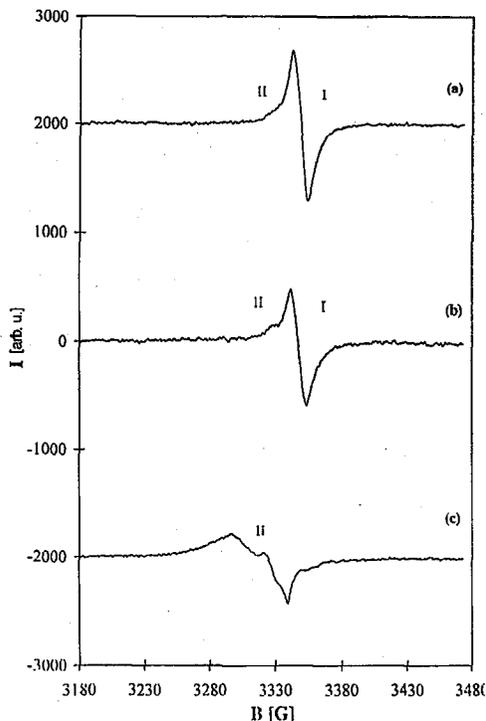


Fig. 4. The X-band EPR spectra of UV-irradiated glasses with the  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (a),  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  (b), and  $\text{Ca}_3\text{Ga}_2\text{O}_6$  (c) compositions, registered at 300 K.

The emission bands of the  $\text{F}^+$  and  $\text{F}$  centres with maxima at about 380 and 620 nm, respectively, were observed in  $\text{CaO}$  crystals under excitation in their absorption bands [21]. The photoexcited emission bands in additively coloured  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  crystals are interpreted as luminescence of the  $\text{F}^+$  centres (a maximum near 450 nm) and the electron-hole recombination on  $\text{Ga}_{\text{tetra}}^{3+}$  antisite defects (a maximum near 360 nm) [7]. The intense luminescence band with a maximum at 390 nm in the  $(\text{SiO}_2\text{-GeO}_2)$  glasses excited by  $\text{N}_2$ -laser is assigned to  $\text{Ge}^{2+}$  ions or structural defects nearly  $\text{Ge}^{2+}$  ions [23].

On the basis of the obtained results and consideration of referenced data for different oxide compounds we suppose that the UV-excited complex broad emission bands with maxima at roughly 500 nm and 420 nm in the  $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$  glasses are due to a release of electrons from oxygen vacancies, which then recombine with an ensemble of the transient  $\text{O}^-$  hole centres [24, 25]. The emission bands with maxima at nearly 380 and 710 nm, which were distinctly revealed in glasses with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{14}$  and  $\text{Ca}_3\text{Ga}_2\text{O}_6$  compositions, may be related with luminescence of two different centres of electron type (analogies of the  $\text{F}^+$  and  $\text{F}$  centres in the crystals of simplest oxides [21]). These assumptions are supported by EPR investigations of the UV-irradiated glasses.

#### 4. Conclusion and acknowledgment

We have found and investigated the intrinsic photoluminescence in the undoped (CaO–Ga<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub>) glasses with different compositions, which are new perspective materials for quantum electronics. In our opinion the complex emission bands are caused by the UV-induced centres of electron type and recombination of the ensemble transient O<sup>-</sup> hole centres. The specific models of luminescence centres and mechanism of intrinsic luminescence in (CaO–Ga<sub>2</sub>O<sub>3</sub>–GeO<sub>2</sub>) glass network may be proposed only after detailed studies of the glass structure and kinetic of emission bands.

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