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Recombination Luminescence in $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ Garnets Doped with Eu^{3+} Ions

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The results of the investigations of X-ray excitation spectra, thermostimulated luminescence and influence of light illumination on the thermoluminescence glow curves of Eu^{3+}-doped $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ garnet polycrystalline samples are presented. It is shown that $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ polycrystalline samples are characterized by intrinsic luminescence, which consists of several components. The nature of intrinsic luminescence is discussed. It is suggested that the nature of thermoluminescence glow peak near 150 K is connected with the $[(V_{Ge}+V_O)^{-}–F^{+}]$ associations formed under X-ray irradiation at 85 K. The influence of light illumination on the TSL intensity of the preliminary X-ray irradiated samples is shown.

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1. Introduction

The complex oxides with garnet structure doped with RE^{3+} (rare earth) ions are important in practical applications as host materials for various phosphors and solid state lasers. The calcium gallium germanium garnet $Ca_3Ga_2Ge_3O_{12}$ doped with Nd^{3+} ions is promising for applications as solid state lasers with diode pumping [1]. These crystals doped with various RE^{3+} ions can be also used as optical pressure sensors, phosphors with near-infrared and long-lasting luminescence properties, etc. [2, 3]. Eu^{3+}-doped $Ca_3Ga_2Ge_3O_{12}$ garnet is interesting material as efficient phosphor with red luminescence [4, 5]. Among the advantages of this material compared with other garnets, is its low melting point ($T_{melt.} = 1370\,°C$), high thermal conductivity, and inhomogeneously broadened lines of absorption and luminescence of the rare earth ions [6, 7]. Nevertheless, the nature of intrinsic radiative recombination and the feature of thermoactivation processes are not sufficiently studied so far in this material. In earlier report [8], we briefly described the spectral-luminescence properties of Eu^{3+}-doped $Ca_3Ga_2Ge_3O_{12}$ polycrystalline ceramic under photoexcitation.

This paper focuses on the analysis of the results obtained by joint consideration of X-ray luminescence spectra, thermostimulated luminescence (TSL) curve and influence of illumination ($\lambda > 600$ nm) on TSL properties to define the trap centers origin and to understand the mechanism of recombination luminescence in pure and Eu^{3+}-doped $Ca_3Ga_2Ge_3O_{12}$ ($x = 0–3$) polycrystals. Besides, to our knowledge, this is the first time, where the influence of light irradiation on the TSL curves of $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ compounds has been studied.

2. Experimental

The polycrystalline ceramic samples of garnet system $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ pure and doped with Eu^{3+} ions were prepared by high-temperature solid-state synthesis. Appropriate amounts of dried CaO, Ga_2O_3 and GeO_2, CdO oxides powders (>99.99% purity on a cation basis) were used as starting materials. The impurities were entered as Eu_2O_3 oxide. The content of europium impurity varies from 0.01 to 0.1 mol.%. Oxide powders were mechanically mixed in agate mortar till we received a homogeneous mass. Pallets were formed by uniaxial pressing of the powders in a steel die (8 mm in diameter) at 150 kg/cm^2 and heated for 10–12 h at ≈ 1150 °C.

To study the phase composition and to determine lattice parameters, X-ray studies of samples were carried out on diffractometer STOE STADI P (Cu K_α-radiation) with the Bragg–Brentano geometry. The analysis of XRD patterns showed that all samples are homogeneous and belong to a cubic garnet single phase (space group *Ia3d*).

All of the observed peaks are characteristic of $Ca_3Ga_2Ge_3O_{12}$ garnet phase and no other phases are detected. The garnet structure contains three types of cationic sites in the lattice: dodecahedral $\{c\}$, octahedral $[a]$, and tetrahedral (d). In calcium gallium germanium garnet, the $\{c\}$, $[a]$, and (d) positions are occupied by Ca^{2+}, Ga^{3+}, and Ge^{4+}, respectively. By replacing Cd^{2+} ions with Ca^{2+} ions, a whole series of solid solutions $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ is formed. The introduction of the divalent Cd^{2+} ions into dodecahedral positions of compound leads to lattice parameter changes between 12.248 Å ($x = 0$) to 12.182 Å ($x = 3$). It can be suggested that incorporated Eu^{3+} impurity ions occupy a lattice site with D_2 symmetry by replacing Ca^{2+} in distorted dodecahedral positions [7, 8]. The excess charge of the Eu^{3+} ions can be compensated by substituting Ge^{4+} ions with Ga^{3+} ions, i.e., by anti-site defects $Ga^{3+}_{(d)}$, as was shown in [9].

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Samples for X-ray emission and TSL investigations were placed in helium cryostat. For temperature control, the UTREKSK-43 system was used. The temperature was set with the accuracy of 0.1 K in the range of 80–500 K. The emission spectra of crystals were measured using the MDR-12 monochromator. Scanning and recording of the X-ray luminescence spectra were carried out with a computerized system. Emission was measured in single photon mode using FEU-51 photomultiplier. X-ray excitation was provided by a URS-55A X-ray generator and Mo-target BSV-2 X-ray tube ($U = 45$ kV, $I = 10$ mA). Samples for TSL investigations were irradiated with X-ray for 5 min at the temperature of liquid nitrogen. TSL curves were obtained in an integrated mode and recorded in a computer database. The spectral composition of TSL curves was registered using the monochromator of an SF-4A spectrophotometer. In the study of the effect of long-wavelength illumination on TSL curves, a 75 W incandescent lamp with a KS-11 ($\lambda = 600-2700$ nm) optical filters was used as an illumination source.

3. Results and discussion

The steady-state X-ray luminescence (XRL) spectra of undoped $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) polycrystalline sample are presented in Fig. 1. XRL spectrum at 85 K is characterized by a complex matrix band peaked at 3.09 eV. The shape of the band and the position of its maximum strongly depend on the temperature. As shown in Fig. 1, maximum of the XRL spectrum shifts to 2.7 eV at 300 K. Asymmetry of luminescence band of XRL spectrum of undoped $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) sample, shift of its maximum in a long-wavelength region with temperature growing demonstrates that it is a superposition of several elementary bands. XRL at 85 K can be decomposed into two elementary Gaussian components with the maxima near 3.26 eV and 2.88 eV (dashed lines show individual components). Upon growing the temperature up to 250 K the 3.26 eV UV band is almost quenched and the intensity of 2.88 eV band is enhanced. At 300 K steady-state XRL spectrum consists of the dominant band with a maximum at 2.82 eV and a weak band at 2.38 eV. This behavior of XRL spectrum can be connected with redistribution of charges between defects under temperature growing. Notice that the steady-state X-ray spectrum for undoped $Ca_3Ga_2Ge_3O_{12}$ ceramics sample correlates with photoluminescence spectra. Similar luminescence band was observed at photoexcitation in band with maxima near 4.9 eV in the region of long-wavelength edge of the fundamental absorption [8].

Figure 2 illustrates the steady-state XRL spectra of $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) samples with 0.01 mol.% Eu^{3+}. XRL at 85 K are characterized with complex matrix band peaked at 400 nm (3.09 eV), the same as in undoped sample and weak Eu^{3+} activator f–f emission lines peaking near 597–620 nm (2.1–2 eV) and 709 nm (1.75 eV). The redistribution of matrix luminescence bands intensity is observed with temperature growing to 300 K. Simultaneously the intensity of the activator emission lines almost does not change. The emission spectra of $Ca_3Ga_2Ge_3O_{12}$:Eu^{3+} at the photoexcitation in the region of long-wavelength edge of the fundamental absorption are characterized by almost the same features [8].

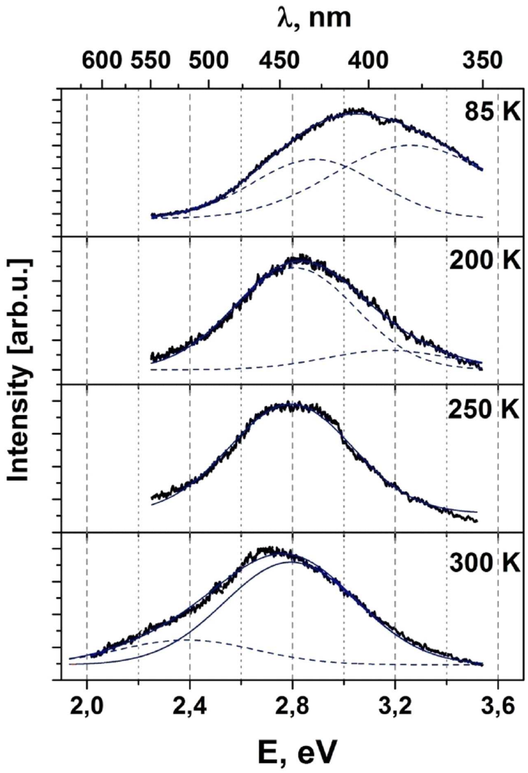

Fig. 1. The steady-state X-ray luminescence spectra of undoped $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) sample in the temperature range 85–300 K. Dashed lines show the decomposition of luminescence spectra into elementary Gaussian components.

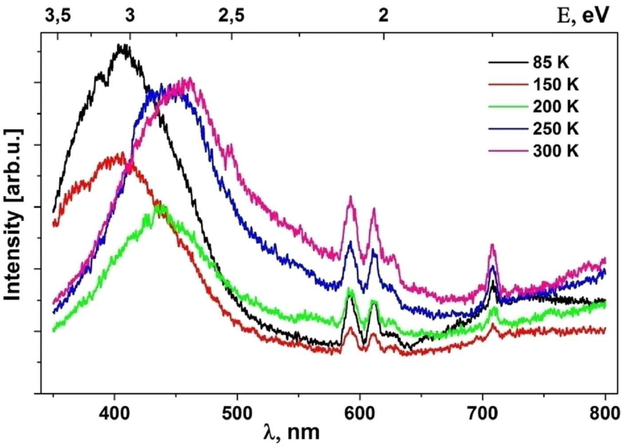

Fig. 2. The steady-state X-ray luminescence spectra of Eu^{3+} doped (0.01 mol.%) $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) polycrystalline sample in the temperature range 85–300 K.

By substitution of Cd^{2+} ions with Ca^{2+} ions, the efficiency of X-ray luminescence increases and reaches maximum for x about 1.5. The steady-state XRL spectrum of $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$:$Eu^{3+}$ ($x = 1.5$) polycrystalline samples at 85–300 K are presented in Fig. 3. The XRL spectra of $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$:$Eu^{3+}$ ($x = 1.5$) samples show broad non-elementary band with maximum near 470 nm (2.6 eV). This band consists of two individual bands with maxima at 2.88 eV (430 nm) and 2.38 eV (520 nm) nm which are strongly overlapped by each other (inset in Fig. 3) and the correlation of intensities between which depends on temperature. The relative increase of band intensity at 550 nm (2.38 eV) was observed at 300 K. The incorporation of Cd in the $Ca_3Ga_2Ge_3O_{12}$ host leads to shifting the absorption edge to longer wavelength and at higher Cd content ($x > 1$) the 380 nm (3.26 eV) band is not observed. Doping with Eu^{3+} leads to appearing activator f–f emission lines in 580–720 nm (2.1–1.7 eV) spectral range, beside intrinsic luminescence bands. The intensity of intrinsic emission decreases under growth of activator ions concentration in samples. In $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 1.5$) sample the intensity of Eu^{3+} luminescence increases by ≈ 1.5 times in comparison with $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) sample.

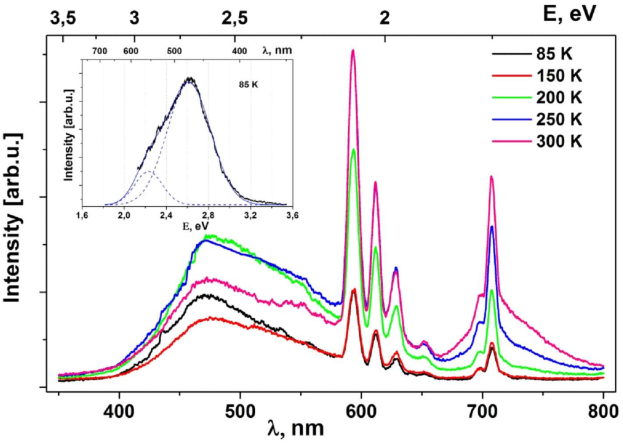

Fig. 3. The steady-state X-ray luminescence spectra of Eu^{3+} doped (0.1 mol.%) $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 1.5$) polycrystalline sample in the temperature range 85–300 K. In the inset the dashed lines show the decomposition of luminescence spectrum at 85 K into elementary Gaussian components.

The intensity of intrinsic luminescence in $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 1.5$) increases approximately twice in comparison with $Ca_3Ga_2Ge_3O_{12}$ garnet. Thus, it is shown that the intrinsic luminescence spectrum of the $Ca_3Ga_2Ge_3O_{12}$ ($Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$)) matrix is a superposition of three elementary bands peaking at 3.26, 2.88, and 2.38 eV. The $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 1.5$) samples show broad non-elementary intrinsic luminescence band consisting of two components with the maxima near 2.88 and 2.38 eV.

Figure 4 illustrates the TSL glow curves of Eu^{3+} (0.01 mol.%) doped $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) sample in the range 120–450 K. Curve 1 in Fig. 4 shows the TSL glow of Eu^{3+} doped sample exposed to X-ray irradiation at 85 K and kept in darkness during 10 min that allowed avoiding afterglow and fading of low-temperature peaks. TSL peaks of Eu^{3+} doped $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) sample are complicated and can be present as a superposition of a few elementary peaks. Beside low-temperature peaks, a few weak peaks in more high-temperature region near 337 and 380 K are detected on TSL glow curve of Eu^{3+} doped $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) ceramics. Curve 2 in Fig. 4 presents TSL glow after X-ray irradiated and an additional illumination of the sample by the light with $\lambda > 600$ nm through the KS-11 filter. Light illumination for 5 min through the optical filter KS-11 of preliminary X-ray irradiated sample at 90 K leads to bleaching of 150 K peak, less of 190 K peak and slightly of 226 K peak. At the same time, no decrease of intensity in 337 and 380 K peaks is observed. From a difference between curves 1 and 2 (curve 3 in Fig. 4) it follows that IR illumination mainly releases the stored light sum, which is characterized by the peak at 150 K. The analysis of 150 K peak has shown that the process of photostimulated release of the stored light sum occurs behind monomolecular kinetics. Spectral composition of low-temperature peaks is mainly characterized by intrinsic emission bands and at high-temperature 337 and 380 K, the activator emission bands dominate.

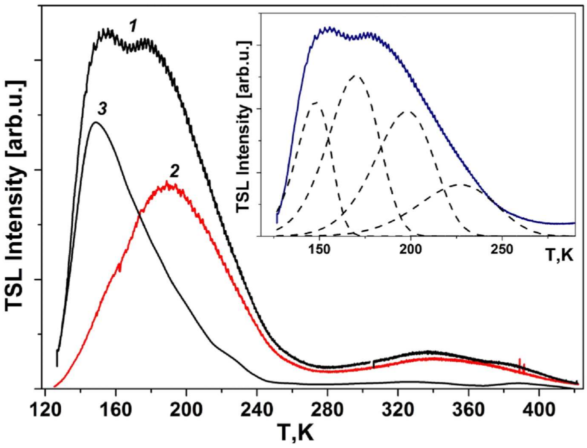

Fig. 4. TSL glow curves of Eu^{3+} doped (0.01 mol.%) $Ca_{3-x}Cd_xGa_2Ge_3O_{12}$ ($x = 0$) sample: 1 — exposed to X-ray excitation during 5 min at 85 K, 2 — after the previous X-ray excitation during 5 min at 85 K and subsequent Illumination by the light with $\lambda \geq 600$ nm (KS-11 filter), 3 — a difference between curves 1 and 2. The inset shows the glow curve deconvolution.

To determine the local level parameters which show up in TSL peak, the decomposition of TL glow curves on elementary compositions was realized by the method of temperature cleaning and using analytical expression for monomolecular kinetics. As follows from inset in Fig. 4, in the TSL glow curves of this sample it is possible to select three dominant elementary peaks at 150, 170, 198 K and weak peak at 226 K in 120–280 K temperature range. The trap depth responsible for the low temperature 150, 190, and 226 K TSL peaks was found to be about 0.16, 0.25, and 0.3 eV, respectively.

The glow curve of $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$:$\mathrm{Eu}^{3+}$ ($x = 1.5$) shows one wide composite intense peak with main maxima at 200 K due to strong broadening and enhanced intensity of low-temperature peaks (Fig. 5). This indicates that the number of structural defects is significantly higher in these samples. Light illumination of preliminary X-ray irradiated sample at 90 K through KS-11 filter strongly decreases the intensity of low-temperature peak near 150 K.

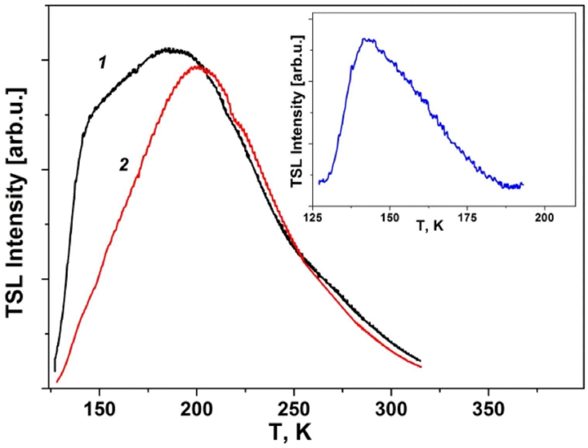

Fig. 5. The TSL glow curves of Eu^{3+} doped (0.1 mol.%) $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ ($x = 1.5$) sample: 1 — exposed to X-ray excitation during 5 min at 85 K, 2 — after the previous X-ray excitation during 5 min at 85 K and subsequent Illumination by the light with $\lambda \geq 600$ nm (KS-11 filter). The inset shows a difference between curves 1 and 2.

It is known that the existence of intrinsic luminescence bands is typical of the complex oxide crystals, in which the oxygen ions occupy low symmetry sites. There are several points of view in the literature regarding their nature, e.g. [10–14]. Often low-temperature luminescence bands are interpreted as radiation decay of self-trapped excitons, which are formed by the relaxation of large radius excitons or in recombination of electrons with holes, localized on their own or impurity defects of the crystal lattice. Some bands of intrinsic luminescence in oxides refer to the emission of anti-site defects or recombination luminescence of active structure defects such as vacancies. Based on the analysis of the obtained results and literature data [12–15] it can be suggested that the low-temperature emission band in the ultraviolet region with the maximum at about 3.2 eV is connected with radiative decay of excitons localized near structural defects of matrix, possibly near the anti-site $\mathrm{Ga}^{3+}_{(d)}$ defects or $\mathrm{Ge}^{3+}_{(d)}$ defect centers. As it was shown in [15] by EPR investigations, the $\mathrm{Ge}^{3+}_{(d)}$ type centers are stable only up to 220 K in single crystals $\mathrm{Ca}_3\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$. Furthermore, a similar temperature behavior is observed for emission band near 3.2 eV, which supports this assumption. The decrease of this intrinsic luminescence intensity near 200–250 K may be related to non-radiative relaxation of electronic excitations and their re-capturing by defect centers.

The probable intrinsic defects in $\mathrm{Ca}_3\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ compound are the oxygen and Ge^{4+} vacancies, because GeO_2 is the most volatile component [7, 15]. Concentrations of the oxygen and cation vacancies in polycrystalline samples, which arise during the high-temperature solid-state synthesis, may be much larger than those in crystals grown in the oxygen atmosphere. The concentration of vacancies additionally increases in $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ samples via a small volatilization of Cd.

Thus, the blue 2.88 eV band, which is also observed in radiation or reducing colored single crystals [11], and green emission band with maximum near 2.25 eV can be related to recombination of donor–acceptor pairs in associative defects $[(\mathrm{V}_{\mathrm{Ge}}\mathrm{V}_{\mathrm{O}})''\text{–}\mathrm{F}^{2+}]$ or $[(\mathrm{V}_{Ga}\mathrm{V}_{\mathrm{O}})''$ - $\mathrm{F}^{+}]$, respectively. It is suggested that combination of O^{2-} and Ge^{3+} vacancies and F-type centers created a more stable type of associates under X-ray irradiation at 85 K, than individual germanium V_{Ge} and oxygen V_{O} vacancies.

Activator recombination luminescence under X-ray excitation observed in the region 580–720 nm is related to the typical ${}^5D_0\text{–}{}^7F_J$ ($j = 1$–4) transitions of Eu^{3+}. The increase of Eu^{3+} luminescence intensity by ≈ 1.5 times in $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ is due to the change of crystal field with entering Cd^{2+} ions into a garnet lattice. It can be noted that under X-ray excitation or excitation at charge transfer band (near 250 nm) both host intrinsic emission and activator luminescence occur and phosphor $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ shows white emission. Phosphor $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ shows brightly red emission under excitation in sharp ${}^7F_0 \rightarrow {}^5L_6$ line of Eu^{3+} ions at 393 nm.

The release of non-equilibrium carriers from shallow traps appears in TSL peaks in the temperature range 120–250 K. Thermostimulated radiative recombination of carriers mainly occurs through the centers responsible for the intrinsic luminescence band in these TSL peaks. Stored energy is released during optical or thermal bleaching. It is suggested that the nature of thermoluminescence glow peaks 150 K and 190 K is connected with the $[(\mathrm{V}_{\mathrm{Ge}}\mathrm{V}_{\mathrm{O}})''\text{–}\mathrm{F}^{2+}]$ or $[(\mathrm{V}_{\mathrm{Ge}}\mathrm{V}_{\mathrm{O}})'\text{–}\mathrm{F}^{+}]$ associations. Thermal or optical destruction of 150 K and 170 K peaks can lead to the appearance of the radiative recombination of donor–acceptor pairs localized on these complex centers. Relatively weak TSL glow peaks were observed within the temperature range 300–400 K. The spectral composition of these TL glow peaks corresponds to Eu^{3+} activator luminescence. It is suggested that the nature of thermoluminescence glow peaks at 336 K and 381 K is connected with recombination within complex centers, which include host defects and Eu^{3+} impurity ions centers.

4. Conclusions

The results of XRL spectroscopy show that luminescence spectra of $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ ($x = 0$–3) polycrystal system depends on Ca/Cd ratio. Particularly, it is shown that $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ ($x = 0$) samples are characterized by two main strongly overlapping bands of a Gaussian shape with maxima at 3.26 and 2.8 eV and a weak band at 2.38 eV. The spectrum of the intrinsic luminescence of $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ ($x = 3$) can be represented by a superposition of two elementary bands with maxima near 2.88 eV and 2.38 eV and total intensity of intrinsic luminescence is increasing approximately twice. It is assumed that the low-temperature UV emission band with maximum at 3.2 eV has an exciton origin and is connected with the radiative decay of excitons localized on cation defect centers. The blue emission band 2.88 eV and green emission band with a maximum near 2.38 eV can be related to recombination of donor–acceptor pairs in associative defects $[(\mathrm{V_{Ge}V_O})''\text{–}\mathrm{F}^{2+}]$ or $[(\mathrm{V}_{Ga}\mathrm{V_O})''\text{–}\mathrm{F}^{+}]$, respectively. The recombination emission of Eu^{3+} ions lines due to the transitions from the excited state $^5D_0$ to split components of ^7F_J ($j = 1$–4) levels is observed on the background intense matrix emission in Eu^{3+} doped $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ polycrystals.

TSL glow curves of Eu^{3+} doped $\mathrm{Ca}_{3-x}\mathrm{Cd}_x\mathrm{Ga}_2\mathrm{Ge}_3\mathrm{O}_{12}$ samples are complicated and can be present as a superposition of a several elementary peaks. It can be assumed that the nature of the low-temperature peaks observed on the TSL curves in the 85–280 K range is connected with intrinsic defects. Particularly, the nature of thermoluminescence glow peak near 150 K can be connected with the $[(\mathrm{V_{Ge}}+\mathrm{V_O})^{-}\text{–}\mathrm{F}^{+}]$ associative centers formed under X-ray irradiation at 85 K. Thermal or optical destruction of this peak can lead to the appearance of the radiative recombination of donor–acceptor pairs localized on these complex centers.

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