Influence of Gold Nanoparticles on Luminescence of Eu^{3+} Ions Sensitized by Structural Defects in Germanate Films

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Abstract

This investigation shows new possibilities of gold nanoparticles using for rise of Ln^{3+} ions luminescence in oxide matrixes at ultra violet synhrotron's excitation on example of germanate films doped with Eu and Au. It has been established that formation of gold nanoparticles (AuNPs) in such films leads to the enhancement of the Eu^{3+} ions luminescence intensity by many times at excitation in broad absorption bands having λ_{max} about 120 and 180 nm. The discovered effect is explained by joint influence of the following factors: (1) rise in the non-bridging oxygen hole centers (NBOHCs) concentration as a result of breakage of the O–Eu bonds in the $\equiv\text{Ge}-\text{O}-\text{Eu}=\text{}$ bridges by the forming AuNPs; (2) nonradiative transfer of excitations from excitons to these centers; (3) effective sensitization of the Eu^{3+} ions luminescence by the centers via the charge transfer (CT) state of the $\text{O}^{2-}+\text{Eu}^{3+}$ complexes; (4) increase in the optical path of the exciting radiation due to the intensification of light scattering by the AuNPs, and, possibly, (5) promoting by the AuNPs of excitations transfer in the exciton–NBOHC–($\text{O}^{2-}+\text{Eu}^{3+}$) system in the nanoparticles field as well as weakening of reverse passivation of the hole centers by the hydrogen atoms formed on the breakage of the end OH^- groups under the action of UV radiation.

Introduction

The use of structural defects of matrix for sensitization of the luminescence of rare-earth ions promises attractive prospects in the cause of creating efficient visualizers of vacuum and solar blind UV radiation (VUV and SBUV). Such visualizers are required for the cosmic radiation detection, long-range detection of forest fires and corona discharges,¹ usage in military engineering and plasma displays,² and a number of other applications. Nevertheless, the information on the sensitization of the Ln^{3+} luminescence by the above-named defects is very limited. Specifically, there are communications on the transfer of electronic excitations from defect centers of silica xerogels,³ and from the Ge-related defects to Tb^{3+} ions in sol–gel-derived glasses,⁴ from surface defects of the SiO_2 nanocrystals to the Eu^{3+} ions in borosilicate glasses,⁵ as well as from matrix to rare-earth ions in $\text{KMLn}(\text{PO}_4)_2:\text{Ln}^{3+}$ (where $\text{M} = \text{Ca}, \text{Sr}$; $\text{Ln} = \text{Y}, \text{La}, \text{Lu}$; $\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}$),⁶ and in $\text{YAlO}_3:\text{Eu}^{3+}$.⁷ However, there is no any information about the enhancement of the Ln^{3+} luminescence, sensitized by structural defects of matrix, on formation of noble metal NP in the matrix. Meanwhile, it is logical to presume that NP formation will increase the concentration of such defects in the matrix and, respectively, the intensity of the sensitized Ln^{3+} luminescence. The latter is especially important in the case of film visualizers. Unfortunately, the use, for this purpose, of the most “budget” variant – the AgNPs – is hardly acceptable due to unavailable presence of the silver ions and clusters in the oxide matrix. Such attributes of the AgNPs interact with the Eu^{3+} ions forming complicated optical centers, and, due to intra-center energy transfer raise the efficiency of the rare-earth activator luminescence excitation by the sun UV radiation outside the limits of the solar blind region ($\lambda \geq 280 \text{ nm}$).⁸ Moreover, as a result of photo-recharging of the silver ions and clusters,⁹ the luminescence efficiency of the Eu–Ag-containing oxide film is not constant. Therefore, in this work we

attempted a study of the influence of the AuNPs, which are practically non-luminescent at excitation by sun UV radiation, on the efficiency of conversion of VUV and SBUV radiation into the visible region of the spectrum in the films of $\text{GeO}_2\text{--Eu}_2\text{O}_3\text{--Au}$ system.

These films were chosen for two reasons. First, the Eu^{3+} ions in dielectric matrices possess strong red luminescence in the $^5D_0 \rightarrow ^7F_j$ transitions that is efficiently excited in the broad and intense CT absorption band whose position may shift in the 3.6–8.2 eV range depending on the nature of the matrix.¹⁰ Second, due to the lower energy of the Ge–O bond, as compared to the Si–O bond,¹¹ it is logical to suppose that the concentration of defects in the GeO_2 matrix will be higher than in the SiO_2 one.

As a result, it has been shown that in the presence of such NP the efficiency of the afore named conversion increases by a few tens of times mainly due to the increase in the concentration of NBOHCs, that efficiently sensitize the Eu^{3+} ions luminescence via the CT state. The other reasons of the efficiency rising is the following: increase in the optical path of the exciting radiation due to the intensification of light scattering by the AuNPs, and, possibly, promoting by the AuNPs of excitations transfer in the exciton–NBOHC–($\text{O}^{2-}+\text{Eu}^{3+}$) system in the nanoparticles field as well as weakening of reverse passivation of the hole centers by the hydrogen atoms formed on the breakage of the end OH^- groups under the action of UV radiation.

Experimental

The films for investigation were formed using layer-by-layer deposition (6 layers) by centrifugation of the GeO_2 sol (5 mass. %, pH = 8.0), containing aqueous solution of HAuCl_4 and a tartrate complex of Eu(III) , onto a silica substrates (KU-1) with air drying of every layer at 300°C during 10 minutes. The final annealing was carried out in the air at different temperatures

T_{an} during 30 minutes. The synthesized films had the following composition (mole %): 100 GeO₂ (film 1), 97GeO₂–3Au (film 2), 90GeO₂–10Eu₂O₃ (film 3) and 87GeO₂–10Eu₂O₃–3Au (film 4). The films thickness was checked with the help of a ‘Talystep’ profilograph-profilometer within $\pm 10\%$ error limits.

The phase analysis was performed with the use of a DRON-2.0 X-ray diffractometer ($\lambda=1.54060 \text{ \AA}$) on the powders obtained from the corresponding film-forming solution by drying and the subsequent heat treatment. The size and form of the nanoparticles were determined with the help of a scanning transmission electron microscope LEO 906E. The optical density spectra (ODS) were recorded with a Cary 500 spectrophotometer. The monitoring of the luminescence spectra (LS) and luminescence excitation spectra (LES) was carried out with the use of pulse-periodic synchrotron radiation (impulse duration is 130 ps, the period is 200 ns) at the SUPERLUMI station of the DESY scientific center (Hamburg, Germany). The acquired spectra were corrected allowing for the spectral sensitivity of the detection system and the distribution of the spectral density of the exciting radiation, respectively, and were expressed as dependences of the number of quanta per unit wavelength interval $dN/d\lambda$ on the wavelength λ . The bandwidth of monochromator slit was 2 nm for both the excitation and monitoring. The identity of the experiment geometry when recording LS and LES enabled sufficiently correct comparison of the intensities of the detected bands in spectra of different films.

IR spectra were recorded using a FTIR Nexus spectrometer (Thermo Nicolet, USA). The samples for these investigations were prepared from powders for which compositions and heat treatment conditions were identical to the corresponding films, by compacting them with KBr. EPR spectra were measured with an ERS-220 (Germany) spectrometer at operational frequency

$\nu = 9.3$ GHz and amplitude of high-frequency (100 kHz) modulation of 0.5 Gs. The determination of the g -factor of detected signal was carried with the use of a certified standard containing the Mn^{2+} ions in ZnS. The position of the resonance line was determined by a maximum of the second derivative spectrum. The correctness of the comparison of intensities for different samples in the IR spectra was ensured by the identical concentration of the powders under study in KBr pellets as well as by the equal thickness of the latter ones.

The luminescence kinetics was investigated with help of a TAC CANBERRA 2145 time amplitude converter at excitation by the synchrotron radiation and by means of a TDS 3032B (Tektronix) digital oscillograph and a H678-20 (Hamamatsu) photomultiplier at excitation by the 4th harmonica of the neodymium laser.

Results

Figure 1 presents the X-ray patterns of the powders studied (**Figure 1a**) and the microphotographs of films (**Figures 1b and 1c**) for $T_{\text{an}} = 800^\circ\text{C}$. Here and below the numbers of curves, correspond to the numbers of the experimental films indicated above or powders of identical composition. According to the data of PDF No. 36-1463, the position and relative intensities of all Bragg reflexes in curve 1 correspond to the hexagonal GeO_2 phase. In curve 2, according to PDF No. 04-0784, there additionally appear reflexes inherent to the Au phase (their position is shown by vertical dotted lines). These reflexes are detected also in curve 4; however, their intensity is essentially lowered. Apart from that, in this curve there are numerous reflexes, a minor part of which coincides by position with the reflexes in curve 3. Microscopic investigation of the obtained films testifies that the GeO_2 and $\text{GeO}_2\text{--Eu}_2\text{O}_3$ films are sufficiently homogeneous while doping of them with gold leads to the formation, at $T \sim 300^\circ\text{C}$, of the AuNPs. With

increasing T_{an} the “diameter” of these nanoparticles in GeO_2 films increases with the simultaneous change of their shape from ellipsoidal to spherical and decrease in polydispersity, whereas, for the $\text{GeO}_2\text{--Eu}_2\text{O}_3\text{--Au}$ film, on the contrary, their diameter decreases. As a result, for $T_{\text{an}} = 800^\circ\text{C}$ the prevailing diameter of the AuNPs in the film 2 amounts approximately 30 nm (**Figure 1b**) and in the film 4 it is lesser by an order of magnitude (**Figure 1c**).

Figure 1. X-ray patterns of powders (a) and microphotographs of films 2 (b) and 4 (c). $T_{\text{an}} = 800^\circ\text{C}$. Intensity of Bragg reflexes in curves 3 and 4 are increased by 1.5 times.

Figure 2 shows the ODS of the synthesized 6-layer films on silica substrate (**Figure 2a**) and those of powders in KBr pellets (**Figure 2b**). The thickness of the films without gold constituted ≈ 200 nm, and in its presence thickness increased by $\approx 20\%$. The spectrum of the substrate practically repeats curve 1a; so, it is not shown in this **Figure**. It is seen that the doping of the

films GeO_2 and $\text{GeO}_2\text{--Eu}_2\text{O}_3$ with gold leads to appearance in the visible region of a band of surface plasmon resonance (SPR) in the AuNPs (**Figure 2a**); the intensity, disposition and shape of this band depend on the film composition and T_{an} (cf. curves 2a, 2'a and 4a, 4'a). At doping of the germinate film with europium, only a slight increase in the intensity of the absorption band at $\lambda \approx 230$ nm is observed. The intrinsic absorption bands of the Eu^{3+} ions are not detected. It is seen from **Figure 2b** that the doping of GeO_2 with gold affects mainly the intensity of vibrational bands of the matrix and insignificantly influences the position of their maxima (cf. curves 1b and 2b). Doping with europium, on the contrary, radically changes vibrational spectra that become practically insensitive to subsequent introduction of gold (cf. curves 3b and 4b).

Figure 2. Optical density spectra of films (a) and powders (b). T_{an} , °C: 300 (2' and 4') and 800 (1–4).

Figure 3 shows the LS of the investigated films of $T_{\text{an}} = 800^\circ\text{C}$ at the excitation wavelength $\lambda_{\text{exc}} = 185$ nm and the temperature of samples 10 K (here and below marked by an asterisk *) and 298 K. It is seen that the spectrum of the 100GeO_2 film (**Figure 3a**) at $T = 10$ K is characterized by two overlapping bands; a broad weakly structured band of $\lambda_{\text{max}} \approx 550$ nm and narrower one, of $\lambda_{\text{max}} \approx 660$ nm. At $T = 298$ K essential weakening of the broad band and, practically, disappearance of the narrow one are observed. For comparison, the spectrum of the substrate obtained at $T = 10$ K (curve 0*) is also presented here. It should be noted that the intensity of the GeO_2 film luminescence rose by a factor of ~ 1.5 during the first two minutes of its excitation at the temperature of 10 K. This effect was absent for other films as well as for all films at room temperature. The spectrum of the $\text{GeO}_2\text{--Au}$ film (**Figure 3b**) at $T = 10$ K is represented by two overlapping broad bands with the maxima at 500 and 610 nm and a relatively narrow intense band of $\lambda_{\text{max}} \approx 685$ nm; at 298 K they transform into a narrow band of $\lambda_{\text{max}} \approx 690$ nm. In the spectrum of the $\text{GeO}_2\text{--Eu}_2\text{O}_3$ film (**Figure 3c**) at $T = 10$ K, only the very weak band of the $^5D_0 \rightarrow ^7F_2$ luminescence of the Eu^{3+} ions is detected; at 298 K it's intensity is increased by a factor of ~ 4.5 . In the spectrum of the $\text{GeO}_2\text{--Eu}_2\text{O}_3\text{--Au}$ film (**Figure 3d**) only the $^5D_0 \rightarrow ^7F_j$ bands of the Eu^{3+} ions are observed, their intensity being approximately 60 times higher, as compared with the film without Au, and also rises by about 4.5 times in passing from $T = 10$ K to $T = 298$ K.

Figure 3. Luminescence spectra of substrate (0) and films (1–4) at $T = 10 \text{ K}$ (marked by *) and $T = 298 \text{ K}$. $\lambda_{\text{exc}} = 185 \text{ nm}$. $T_{\text{an}} = 800 \text{ }^{\circ}\text{C}$.

Figure 4 shows the LES of the investigated films of $T_{\text{an}} = 800^{\circ}\text{C}$ and that of the substrate used at different recording wavelength (λ_{rec}). It is seen that they are represented by two weakly

overlapping broad bands which position and relative intensities differently depend on the composition and the temperature of the film. In the case of the GeO₂ film these bands are characterized by $\lambda_{\text{max}} \approx 125$ nm and $\lambda_{\text{max}} \approx 180$ nm, and their relative intensities undergo inversion on changing T from 10 K to 298 K (**Figure 4a**). For the GeO₂–Au film the spectra at the two temperatures and recording in the narrow intense luminescence band are practically coincident, and the intensity of the short-wavelength band considerably prevails over that of long-wavelength band (**Figure 4b**). At recording in the range of the broad luminescence band appearing at $T = 10$ K, an additional weakly structured broad band arises in the LES of this film having $\lambda_{\text{max}} \approx 230$ nm and a shoulder at $\lambda \approx 260$ nm (**Figure 4b**, insert). In the spectrum of the GeO₂–Eu₂O₃ film, the temperature redistribution of the bands relative intensities is not considerable; however, at $T = 298$ K the long-wavelength band is noticeably shifted to the red, and the appearance of a sloping “wing” in the 215–250 nm range is observed (**Figure 4c**). The particularity of the excitation spectrum of the GeO₂–Eu₂O₃–Au film is the radical redistribution of the relative intensity for the benefit of the long-wavelength band (**Figure 4d**).

Figure 4. Luminescence excitation spectra of substrate (0) and films (1–4) at $T = 10 \text{ K}$ (marked by *) and $T = 298 \text{ K}$. λ_{rec} , nm: 550 (1a, 1*a) and 665 (0*a); 615 (c, d); 690 (b) and 500 (b, insert). $T_{\text{an}} = 800 \text{ }^\circ\text{C}$.

Discussion

The analysis of the X-ray patterns presented in **Figure 1a** shows that, on doping the GeO_2 film by europium tartrate in the case of $T_{\text{an}} = 800^\circ\text{C}$, the initial crystalline phase undergoes essential changes (cf. curves 1 and 3). Since, on such doping, the K and Na ions are incorporated into the germanium dioxide matrix together with Eu ions, we can suppose, taking into account the reference values of the interplanar spacing in germanates of the mentioned elements, that the numerous reflexes in curves 3 and 4 are caused by germanates of different composition and structure. The doping with gold practically does not change the structure of the GeO_2 film, adding into the corresponding X-ray patterns only reflexes that correspond to gold phase, but it affect substantially the structure of the $\text{GeO}_2\text{--Eu}_2\text{O}_3$ film. In the latter case considerably decrease (by an order of magnitude) in the diameter of the AuNPs for the $\text{GeO}_2\text{--Au}$ film doped with europium (cf. **Figures 1b** and **1c**) may be associated with the decrease in its free volume due to the formation of abovementioned germanates.

The temperature behavior of the shape and dimensions of the AuNPs, described in considering **Figure 1**, correlates well with the presented ODS (**Figure 2a**). Indeed, using the known methods of derivative spectroscopy, it is easy to show that SPR band in curve 2' represents two elementary bands having $\lambda_{\text{max}} \approx 530$ and 740 nm caused by the excitation of surface plasmons along the shorter and longer axis of an ellipsoid. It should be noted that the increase in optical density on the short-wavelength side of the SPR band by many times with decrease λ for the $\text{GeO}_2\text{--Au}$ film (curve 2) as compared to the $\text{GeO}_2\text{--Eu}_2\text{O}_3\text{--Au}$ one (curve 4) is explained by the rise of the interband absorption intensity with the increase in the AuNPs diameter. As regards the

slight intensity rise in the band at $\lambda \approx 230$ nm on doping the GeO₂ film with europium, it is logical to associate in with a CT band of O²⁻+Eu³⁺ complexes.

The vibrational bands at 875 and 700 cm⁻¹, which are typical for the 4-coordinated and 6-coordinated Ge⁴⁺ ions, respectively,¹² are present in the IR spectrum of the GeO₂ powder (**Figure 2b**, curve 1) only as shoulder of more intense band that testifies to its essential structure imperfection. In particular, by analogy with Ref.¹³ where it was established that, on the breakage of the Si–O–Si bond, the corresponding vibrational band is shifted to lower frequencies, the strong band of $\nu_{\max} \approx 850$ cm⁻¹ may be assigned to vibrations of the Ge–non-bridging oxygen bonds in the [GeO₄] groupings, while the weak shoulder at 880 cm⁻¹ and the band at 960 cm⁻¹ may be attributed to the ν_3 vibrational mode of these groupings.¹⁴ The essential increase in the intensity of these shoulder and band, as well as that of the triplet of $\nu_{\max} \approx 519, 554,$ and 584 cm⁻¹, typical for the hexagonal phase of GeO₂,¹⁵ on doping with gold (**Figure 2b**, curve 2) testify to the rise in the concentration of the corresponding structural fractions. Drastic shift of these bands to lower frequencies and appearance of new ones on doping GeO₂ and GeO₂–Au powder with europium (**Figure 2b**, curves 3 and 4) seem to be associated with the formation of the europium germanate phase. Thus, the synthesized films must possess defects that are characteristic for GeO₂ of both coordination states of Ge⁴⁺ ions and also for europium germanates.

Before passing to the analysis of the spectral-luminescent properties of the synthesized films, we note that for the SiO₂ and GeO₂, which are structural analogues, the most typical luminescent defects are the NBOHCs ($\equiv\text{Si}-\text{O}^\bullet$ and $\equiv\text{Ge}-\text{O}^\bullet$) and the oxygen-deficient centers (ODCs). It is accepted to subdivide the latter into ODCs(II) that are oxygen double vacancies ($=\text{Si:}$ and $=\text{Ge:}$)

and ODC(I) the nature of which is not quite clear. A number of researchers,¹⁶ are inclined to the opinion that ODCs(I) are oxygen monovacancies ($\equiv\text{Si}-\text{Si}\equiv$ and $\equiv\text{Ge}-\text{Ge}\equiv$) or multivacancies, whereas in Ref.¹⁷ it is proposed to consider them as oxygen vacancies localized in octahedral structured motive. NBOHCs in the structural motive of vitreous SiO_2 are characterized by a relatively narrow luminescence band of $\lambda_{\text{max}} \approx 650$ nm that is excited in the low-intensity resonance band and in the intense band of $\lambda_{\text{max}} \approx 260$ nm.¹⁸ In Ref.¹⁹ it is shown that the strong absorption band of $\lambda_{\text{max}} \approx 180$ nm also belongs to these centers. At passing to vitreous GeO_2 , the NBOHC luminescence shifts to 690 nm.²⁰ The ODCs are responsible for the luminescence bands at 280 nm (the $S_1 \rightarrow S_0$ transition) and 460 nm (the $T_1 \rightarrow S_0$ transition) excited at 180 nm ($S_0 \rightarrow S_2$), 240 nm ($S_0 \rightarrow S_1$), and 330 nm ($S_0 \rightarrow T_1$).¹⁶ Only the absorption band of $\lambda_{\text{max}} \approx 180$ nm is assigned to ODCs(I) by some authors; at excitation in this band the transformation of ODC(I) into ODC(II) is possible.¹⁶ In vitreous GeO_2 ODCs(II) are characterized by luminescence bands of $\lambda_{\text{max}} \approx 300$ nm (the $S_1 \rightarrow S_0$ transition) and 420 nm (the $T_1 \rightarrow S_0$ transition) which are efficiently excited in the $S_0 \rightarrow S_1$ absorption band at 250 nm.²¹ Furthermore, in the LSs of SiO_2 and GeO_2 a band at $\lambda \approx 500$ nm may be observed that belongs to autolocalized exciton characterized by the absorption bands at 190 and 120 nm.^{22, 23} The spectral-luminescent properties of defect centers in the structural motive of 6-coordinated silicium and germanium are studied to a lesser degree. In particular, it is established that rutil-like crystals of GeO_2 with an admixture of Na and germanate glasses of analogous composition are characterized by similar ODCs, modified by sodium, having luminescence bands at 420 nm ($S_1 \rightarrow S_0$) and 540 nm ($T_1 \rightarrow S_0$).²⁴

Considerable distinctions in the LSs and LESeS of the films studied and those of the silica substrate (**Figures 3** and **4**; compare curves I^*-4^* with curve 0^*) show that the contribution of this latter to the luminescence of doped films is not essential. The substrate contribution, as a relatively narrow luminescence band of $\lambda_{\max} \approx 650$ nm that is typical for NBOHCs, is probable only in the LS of the GeO₂ film (**Figure 3a**, cf. curves 0^* and 1^*). The broad luminescence band of $\lambda_{\max} \approx 550$ nm observed for this film is not likely to be a superposition of the $T_1 \rightarrow S_0$ bands, belonging to modified ODCs, because in the LESeS (**Figure 4a**, curves 1 and 1^*) the intense $S_0 \rightarrow S_1$ band of such centers at $\lambda \sim 240$ nm is absent. Therefore, attempting to the interpretation of this luminescence band, one should take into account the increase in the intensity by a factor of 1.5 in the process of stationary excitation at $T = 10$ K noted in describing **Figure 3a**. As it is known,²⁵ on passivation of 2-coordinated silicon by molecular hydrogen the non-luminescent $=\text{Si}:\text{H}_2$ centers are formed. However, in the process of their excitation by radiation in the 180–200 nm range at $T < 80$ K, there occur the elimination of H₂ from the silicon atom and the appearance of subsequent recombination luminescence of the $=\text{Si}:\dots\text{H}_2$ centers with spectrum different from the LS of the $=\text{Si}:$ centers.¹⁷ Allowing for these facts, it is natural to suppose that in our case analogous situation takes place.

It is to be noted that the films obtained with the use of the sol-gel method are characterized by high concentration of the impurity OH[−] groups. In particular, for silica films with $T_{\text{an}} = 300^\circ\text{C}$, the concentration of such groups is up to 60 mass %.²⁶ Naturally, with the rise in T_{an} , it is lowered; however, judging from the sufficiently intense band at $\nu \approx 3400$ cm^{−1} in **Figure 2b** that belongs to stretching vibrations of the OH[−] groups, it remains essential at $T_{\text{an}} = 800^\circ\text{C}$ as well. Therefore, the passivation of structural defects by these groups is quite plausible, and it may proceed according to the following reactions:

Evidently, the passivated centers formed by the reaction (2) during the synthesis of the GeO_2 film photo-dissociate at the excitation used according to the reaction

and after that undergo radiative recombination. In addition, a contribution to the broad luminescence band at $\lambda_{\text{max}} = 550$ nm can be made also by autolocalized excitons which is confirmed by the presence of a broad band at 125 nm in its LES (**Figure 4a**). The observed inversion of the intensity of bands in the LESes on rising T from 10 K to 298 K (**Figure 4a**, cf. curves I and I^*) does not contradict to the proposed interpretation because the temperature rise leads to reverse passivation of luminescent defects. Also, it should be taken into account that there is a considerable fraction of silicon $\equiv\text{SiSiSi}\equiv$ nanocrystallites in nonstoichiometric silica glasses characterized by the luminescence and luminescence excitation bands at $\lambda \approx 540$ nm and 190 nm, respectively.²⁷ This allows one to suppose that in the GeO_2 films the formation of similar germanium nanocrystallites is also possible, and they may make their contribution to the LSes and LESes under consideration as well. As regards the contribution of NBOHCs to the luminescence of this film, it is not large judging by the data of **Figure 3a**.

The broad and relatively strong two-humped band in the LS of the GeO_2 -Au film having λ_{max} at ~ 500 and ~ 600 nm detected at $T = 10$ K (**Figure 3b**), in our opinion, is due mainly to the $T_1 \rightarrow S_0$ transition of the $=\text{Ge}\cdot$ centers that is promoted by the AuNPs.²⁸ The appearance of the intense $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ bands at 235 and 190 nm and weak $S_0 \rightarrow T_1$ band at 330 nm (**Figure**

4b, see insert), characteristic for ODCs(II), in the LES of this band is the evidence in favor of such interpretation. In this case it is logical to explain the spectral gap at $\lambda \approx 540$ nm on the luminescence band under consideration by the absorption in the SPR band (cf. **Figures 2a** and **3b**, curves 2 and 2*, respectively). “Photolysis” ODCs formed by the reaction (4) should also make a certain contribution to this luminescence band but the available data are insufficient for its distinguishing. It is necessary to note that, in the discussed spectral region, the AuNPs,^{29, 30} and centers of the type of $[\equiv\text{Ge}-\text{O}-\text{Au}_2]^-$ whose silica analogues are described in Ref.³¹ are also luminescent. However, the disappearance of the two-humped luminescence band under consideration at $T = 298$ K allows one to neglect its contribution.

The narrow luminescence bands of $\lambda_{\text{max}} \approx 685$ nm at $T = 10$ K and $\lambda_{\text{max}} \approx 690$ nm at $T = 298$ K (**Figure 3b**) are similar in shape and position to the band of the $\equiv\text{Ge}-\text{O}^\bullet$ centers.²⁰ However, the absence in their LESes (**Figure 4b**) of the intense band at 260 nm and much greater intensity of the 120 nm band as compared to 180 nm band, may be the evidence of a predominant contribution to this band of autolocalized excitons. Note that sufficiently intense band of the luminescence of the latter at 690 nm was already observed for germanate glasses,³² but its half-width was essentially larger than in our case. Probably, here effective sensitization of the $\equiv\text{Ge}-\text{O}^\bullet$ centers by autolocalized excitons takes place. As follows from the conservation at $T = 10$ K and 298 K of the relative intensities of the excitation bands at 120 nm and 180 nm of the narrow-band luminescence considered (**Figure 4b**, cf. curves 2 and 2*), such sensitization proceeds by resonance energy transfer. Since the luminescence of NBOHC is prone to considerable temperature quenching,^{18, 33, 34} noticeable increase in the intensity of their luminescence at $T = 298$ K (**Figure 3b**) may indicate either to the lowering of non-radiative

losses in the populating of the luminescent state in presence of AuNPs, and/or to the binding of the hydrogen atoms liberated according to the reaction:¹⁹

Such binding seems to be possible as a result of photocatalytic evolution of $\text{H}^{\bullet}$ to a molecular state on the AuNPs surface.^{35–37} As regards the observed structure of the $\equiv\text{Ge}-\text{O}^{\bullet}$ centers luminescence band (shoulders at $\lambda \approx 695$ nm and 725 nm), it may be associated with the existence of surface and bulk centers and the splitting of the ground state of the latter resulting from the lowering of symmetry due to the Jahn-Teller effect.³⁸

At last, the complete substitution of the considered luminescence bands of the GeO_2 and GeO_2 -Au films, on doping with europium, by the $^5D_0 \rightarrow ^7F_j$ bands of the Eu^{3+} ions (cf. **Figures 3a** and **3b** with **3d**) give evidence of the efficient transfer of excitations from the VUV energy donors to the rare-earth activator. The essential increase in the efficiency of this transfer on rising T (**Figures 3** and **4**, cf. curves 3^* and 3 , 4^* and 4) allows us to conclude that the transfer is realized via the CT state $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$. Assuming that the disposition of the energy states of the GeO_2 film and $\equiv\text{Ge}-\text{O}^{\bullet}$ centers is similar to that calculated in Ref.³⁹ for the $(\text{OH})_4\text{Si}$ and $(\text{OH})_3\text{Si}-\text{O}^{\bullet}$ clusters, we may propose the scheme depicted in **Scheme 1** for the description of the prevalent processes of sensitization of the Eu^{3+} ions luminescence in the films studied. According to this **Scheme**, absorption of radiation in the bands of $\lambda_{\text{max}} \approx 125$ and 150 nm (indicated by solid lines) leads to production of electron-hole pairs whose recombination is accompanied by the nonradiative energy transfer (indicated by dashed line) to NBOHCs. In this case, transfer of electrons occurs from the lone-pair $n(\text{O}_b)_{\parallel}$ orbitals, that are oriented parallel to the corresponding $\text{Ge}-\text{O}_b-\text{H}$ planes in the $(\text{OH})_3\text{Ge}-\text{O}^{\bullet}$ cluster, to the $n(\text{O}_{\text{nb}})_y$ level with one

unpaired electron. The same transition is realized at excitation in the band of $\lambda_{\max} \approx 180$ nm. Subsequent nonradiative energy transfer proceeds due to the following electron transitions $n(\text{O}_{\text{nb}})_y \rightarrow n(\text{O}_{\text{b}})_{\parallel} : \text{GSCT} \rightarrow \text{ESCT}$, where GSCT and ESCT are ground and excited states of the CT complex $\text{O}^{2-}+\text{Eu}^{3+}$. Then electron passes to upper excited states of the rare-earth ion with simultaneous return of an electron from the ground state of this ion to the GSCT. The energy transfer to the rare-earth ion by transition from the $n(\text{O}_{\text{nb}})_y$ level of an NBOHC to the $n(\text{O}_{\text{b}})_{\perp}$ orbitals, located 38400 cm^{-1} lower and oriented perpendicular to the $\text{Ge}-\text{O}_{\text{b}}-\text{H}$ plane, is impossible since it requires borrowing considerable amount of energy from the matrix. Naturally, similar transfer by transition from the $n(\text{O}_{\text{nb}})_y$ level to the σ -bonding orbital $\sigma(\text{Ge}-\text{O}_{\text{nb}})_z$ is impossible too. The direct energy transfer to the $\text{O}^{2-}+\text{Eu}^{3+}$ complexes from electron-hole pairs formed at absorption from all valence subbands, judging from low intensity in LESes of the $\text{GeO}_2-\text{Eu}_2\text{O}_3$ film (**Figure 4c**), is inefficient. It is appropriate to emphasize here that absence in LESes of the $\text{GeO}_2-\text{Eu}_2\text{O}_3-\text{Au}$ film absorption bands caused by the $=\text{Ge}\cdot$ centers (cf. **Figure 4d** and insert in **Figure 4b**) testifies dramatic exceeding of efficiency of energy transfer from excitons and NBOHCs to the $\text{O}^{2-}+\text{Eu}^{3+}$ complexes over transfer to the $=\text{Ge}\cdot$ centers.

Scheme 1. Energy states and prevalent processes of the Eu^{3+} ions luminescence sensitization. Designations are explained in the text.

The increase by many times in the luminescence intensity of the $\text{GeO}_2\text{--Eu}_2\text{O}_3\text{--Au}$ film at $T = 298 \text{ K}$, as compared to the $\text{GeO}_2\text{--Eu}_2\text{O}_3$ film (cf. **Figure 3d** and **3c**), makes it possible to conclude that (1) at this temperature the rate of the Eu^{3+} luminescence sensitization by the $\equiv\text{Ge-O}^\bullet$ centers exceeds the rate of the de-excitation of the latter in the absence of europium, and (2) the formation of the AuNPs in the covalently bound $\equiv\text{Ge-O-Ge}\equiv$ net drastically facilitates its breakage with the formation of NBOHCs. Radical increase in the concentration of the latter in the presence of AuPNs is also confirmed by the EPR spectra (**Figure 5**) from which it is seen that the integral intensity of the signal of $g \approx 2.002$ that caused by the $\equiv\text{Ge-O}^\bullet$ centers^{40,41} in the presence of AuNPs is higher about 9 times in comparison with GeO_2 film. However, in comparison with the $\text{GeO}_2\text{--Eu}_2\text{O}_3$ film this rise proves to be only approximately 2.5 times and cannot lead to the observed rise of the Eu^{3+} luminescence intensity by 60 times.

Figure 5. EPR spectra of powders. $T_{\text{an}} = 800\text{ }^{\circ}\text{C}$, $T = 298\text{ K}$.

The observed enhancement of the Eu^{3+} sensitized luminescence may have an additional reason – namely the increase in the optical path of the exciting radiation due to light scattering introduced by metallic NPs.⁴² With the aim of elucidation of the contribution of this factor we have analyzed the behavior of the luminescence of Eu-containing films with gold and without it, at excitation in the Eu^{3+} ion own absorption bands (**Figures 6a** and **6b**), and carried out a calculation of the dependences of the factors of scattering Q_{sca} , absorption Q_{abs} and extinction Q_{ext} on wavelength (**Figure 6c**) on the basis of the Mie theory for AuNPs of diameter equal to 30 nm by the known method.⁴³

Figure 6. Luminescence (a), luminescence excitation (b) and calculated factors of scattering, absorption and extinction (c) spectra. $\lambda_{exc} = 395 \text{ nm}$ (a), $\lambda_{rec} = 612 \text{ nm}$ (b). $T_{an} = 800 \text{ }^\circ\text{C}$, $T = 298 \text{ K}$.

As seen from this **Figure**, in the presence of AuNPs and at excitation in the ${}^7F_0 \rightarrow {}^5L_6$ band ($\lambda = 395 \text{ nm}$), an increase in the intensity of the Eu^{3+} luminescence by about two times takes place (**Figure 6a**, cf. curves 3 and 4). This enhancement exceeds by an order of magnitude the

increase in the film thickness on the incorporation of gold, which allows one to connect it with the increase in light scattering for exciting radiation. In this case the intensities of luminescence excitation bands ${}^7F_0 \rightarrow {}^5D_2$ ($\lambda \approx 465$ nm) and ${}^7F_0 \rightarrow {}^5D_1$ ($\lambda \approx 530$ nm) increase by factors of 1.7 and 1.3, respectively, and, at excitation in the CT band ($\lambda \approx 250$ nm), by a factor of 2.6 (**Figure 6b**, curves 3 and 4). These results satisfactorily correlate with the dependence $Q_{\text{sca}}(\lambda)$ with the exception of the range about $\lambda \approx 530$ nm (cf. **Figure 6b** with **Figure 6c**) which may be explained by the screening of the ${}^7F_0 \rightarrow {}^5D_1$ band by the SPR band. Here it should be noted that, according to the carried-out calculation, the Q_{sca} value quickly decreases with reduction of diameter of AuNPs and at the diameter of 10 nm and lesser light scattering practically disappears, i. e. it is caused by only rather large agglomerates of the NPs for the $\text{GeO}_2\text{--Eu}_2\text{O}_3\text{--Au}$ film. Taking into consideration the weak change of Q_{sca} in spectral range of 200–250 nanometers, we can believe that the rise of the efficiency of excitation in the absorption band of the NBOHCs due to light scattering does not exceed a factor of 3.

For completeness of our research we have carried out studying of luminescence kinetics of the considered structural defects which shows that the mean values of duration of its decay ($\bar{\tau}$) at $T = 10$ K and $\lambda_{\text{rec}} = 450, 550,$ and 650 nm constitute, respectively, 3.7, 2.5, and 1.4 ns for the GeO_2 film (see **Figure 7a**). For the $\text{GeO}_2\text{--Au}$ film the luminescence kinetics at the indicated λ_{rec} is accelerated by, approximately, 10–20 %. It was not possible to measure correctly the $\bar{\tau}$ value at $\lambda_{\text{rec}} = 690$ nm since it exceeds by an order of magnitude the pulse-repetition interval of synchrotron radiation. The decay of luminescence of the Eu^{3+} ions in the $\text{GeO}_2\text{--Eu}_2\text{O}_3$ film occurs by a law close to exponential (**Figure 7b**, curve 3) with the $\bar{\tau}$ equal to 1260 μs . For the

GeO₂–Eu₂O₃–Au film, the decay is nonexponential (**Figure 7b**, curve 4), however, its $\bar{\tau}$ increases to 1550 μ s.

Figure 7. Kinetics of decay for the luminescence of (a) structural defects and (b) Eu³⁺ ions.

$T_{an} = 800$ °C. λ_{exc} , nm: (a) 185 and (b) 266. T , K: (a) 10 and (b) 298.

These results do not contradict the identification of the luminescing structural defects stated above and allow to believe that sensitization of the Eu³⁺ ions luminescence proceeds under conditions of strong interaction with rates that are essentially larger than $1 \cdot 10^9$ s⁻¹. The increase in the probabilities of the optical transitions in the Eu³⁺ ions, caused by the electromagnetic interaction with the AuNPs, is absent. Therefore, as the main reason of drastic enhancement of the sensitized Eu³⁺ luminescence on the AuNPs formation is (1) the primary breakage of the

Eu–O bonds as weaker bonds in the Ge–O–Eu “bridges” and creation of complicated centers including the europium ions and the NBOHCs and characterized by the efficient transfer of excitations and/or (2) promoting by the AuNPs of excitations transfer in the exciton–NBOHC–($\text{O}^{2-}+\text{Eu}^{3+}$) system in the nanoparticles field. The bonding force calculation for the $\text{Ge}^{4+}-\text{O}^{2-}$ and $\text{Eu}^{3+}-\text{O}^{2-}$ chemical bonds on the basis of electronegativity by the method⁴⁴, that gives the values of 1.52 and 1.25 relative units, respectively, that testifies to benefit of the first supposition. For benefit of the second supposition witnesses significant increase in relative intensity of the “exciton” band in **Figure 4b** and results of work⁴⁵ where it is shown that the local field of noble metals NPs with diameters realized in our experiment manifold exceeds the incident wave field.

It is to be noted here that the AuNPs, apart from the considered positive influence on the intensity of sensitized luminescence of the Eu^{3+} ions, are also their relatively efficient quenchers.⁴⁶ Therefore, in the development of similar films for visualization of VUV and SBUV radiation, the optimization of the concentration of gold and of the dimensions of its NPs represent a great value.

Conclusions

The GeO_2 films obtained with the help of the sol-gel method, at excitation in the vacuum and solar-blind regions of UV radiation, manifest weak luminescence that is due mainly to the $=\text{Ge}:\dots\text{H}_2$ centers resulting from the photo-dissociation of the $=\text{Ge}:\text{H}_2$ centers, passivated by impurity hydroxyl groups, and to autolocalized excitons. Doping of the GeO_2 films with the salt HAuCl_4 is accompanied by the formation of the AuNPs that leads to breakage of the bridge bonds of its structural framework and to drastic, by many times, rise in the concentration of the

NBOHC. The $\text{GeO}_2\text{--Au}$ films exhibit far more intense luminescence that is due, at $T = 10$ K, mainly to the $T_1 \rightarrow S_0$ transitions, promoted by the AuNPs, in the $=\text{Ge}:$ centers, to autolocalized excitons, and to the NBOHCs. At $T = 298$ K the luminescence spectrum of such film is presented only by the intense band caused by the NBOHCs. The doping of the GeO_2 film with europium results in the disappearance of the luminescence of structural defects and that of autolocalized excitons and in the appearance of weakly intense sensitized luminescence of the Eu^{3+} ions. The sensitization is performed by means of nonradiative energy transfer in the exciton–NBOHC–($\text{O}^{2-}+\text{Eu}^{3+}$) system, where transfer of energy in the latter link is performed from a high-excited state of the NBOHCs to the CT state of complexes $\text{O}^{2-}+\text{Eu}^{3+}$ in which excitation of the rare earth ion is occurred by means of electron transfer. Efficiency of such sensitization increases by many times for the $\text{GeO}_2\text{--Eu}_2\text{O}_3\text{--Au}$ film. Simultaneously, luminescence bands characteristic for the $\text{GeO}_2\text{--Au}$ film disappear. The possible reasons of such increase are (1) rise in concentration of NBOHCs as a result of a breakage of the Eu--O bonds in the bridges Ge--O--Eu and creation of complicated centers including the Eu^{3+} and NBOHC; (2) increase in the optical path of the exciting radiation due to the intensification of light scattering by the AuNPs, and, possibly, (3) promoting by the AuNPs of excitations transfer in the exciton–NBOHC–($\text{O}^{2-}+\text{Eu}^{3+}$) system in the nanoparticles field as well as weakening of reverse passivation of the hole centers by the hydrogen atoms formed on the breakage of the end OH^- groups under the action of UV radiation.

The acquired results manifest that the use of noble metals NPs for the raising of the non-bridging oxygen hole centers concentration in oxide matrices and the sensitization of luminescence of rare-earth activators by these centers is a very promising approach. The effect under

consideration may be used for drastic increase of the efficiency of conversion of the vacuum and solar blind ultraviolet radiation into the visible region of the spectrum.

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Figure 1. X-ray patterns of powders (*a*) and microphotographs of films 2 (*b*) and 4 (*c*).

$T_{\text{an}} = 800^{\circ}\text{C}$. Intensity of Bragg reflexes in curves 3 and 4 are increased by 1.5 times.

Figure 2. Optical density spectra of films (a) and powders (b). T_{an} , °C: 300 (2' and 4') and 800 (1–4).

Figure 3. Luminescence spectra of substrate (0) and films (1–4) at $T = 10$ K (marked by *) and $T = 298$ K. $\lambda_{\text{exc}} = 185$ nm. $T_{\text{an}} = 800$ °C.

Figure 4. Luminescence excitation spectra of substrate (0) and films (1–4) at $T = 10 \text{ K}$ (marked by *) and $T = 298 \text{ K}$. λ_{rec} , nm: 550 (1a, 1*a) and 665 (0*a); 615 (c, d); 690 (b) and 500 (b, insert). $T_{\text{an}} = 800 \text{ }^\circ\text{C}$.

Scheme 1. Energy states and prevalent processes of the Eu^{3+} ions luminescence sensitization.

Designations are explained in the text.

Figure 5. EPR spectra of powders. $T_{\text{an}} = 800\text{ }^{\circ}\text{C}$, $T = 298\text{ K}$.

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