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# OPTICAL PROPERTIES

# Influence of Silver on the Sm<sup>3+</sup> Luminescence in "Aerosil" Silica Glasses

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**Abstract**—The introduction of silver into the samarium-containing silica glasses prepared by the original solgel method leads to the formation of complex optical centers involving samarium ions and simple and/or complex silver ions. These centers are characterized by the effective sensitization of  $\text{Sm}^{3+}$  luminescence by Ag<sup>+</sup>,  $(\text{Ag}_2)^+$ , and  $(\text{Ag}^+)_2$  ions according to the exchange mechanism for, at least,  $\text{Sm}^{3+}-\text{Ag}^+$  centers. The formation of Sm–Ag centers is accompanied by an increase in the concentration of nonbridging oxygen ions, which prevent the reduction of silver ions by hydrogen. Silver nanoparticles formed in small amounts upon this reduction are effective quenchers of luminescence from the corresponding excited states of  $\text{Sm}^{3+}$  ions.

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# 1. INTRODUCTION

As is known, Sm<sup>3+</sup> and Sm<sup>2+</sup> ions in oxide matrices can exhibit an intense luminescence in the visible spectral range upon transitions from the  ${}^{4}G_{5/2}$  and  ${}^{5}D_{0}$  states, respectively [1, 2]. Moreover, Sm<sup>3+</sup> ions are characterized by the absence of induced absorption (from the metastable state) in the range of potential laser transitions, and Sm<sup>2+</sup> ions can be effectively oxidized upon excitation within the  ${}^{6}H_{5/2} \longrightarrow {}^{5}D_{0}$  transition. As a consequence, Sm<sup>3+</sup> and Sm<sup>2+</sup> ions can be treated as activators for lasers in the visible range [3] and for optical media used for ultradense data storage [4], respectively. However, there are substantial disadvantages when these ions are used for the above purposes. For example, very low-intensity "operating" absorption bands are characteristic of samarium ions. It seems likely that this disadvantage can be somewhat minimized using an appropriate luminescence sensitizer or the observed effect of an increase in the probability of optical transitions of the activator in the vicinity of metal nanoparticles for the spectral bands coinciding with the surface plasmon absorption band (see, for example, [5–7]). It should be noted that our recent attempt [8] to reveal this effect in films of the GeO<sub>2</sub>-Eu<sub>2</sub>O<sub>3</sub>-Âu system did not meet with success. Furthermore, we also failed to observe the aforementioned effect in GeO<sub>2</sub>-Eu<sub>2</sub>O<sub>3</sub>-Ag films [9], in which an increase in the Eu<sup>3+</sup> luminescence intensity was provided by the effective sensitization with silver ions and  $(Ag_n)^{m+}$  oligometric clusters located at the surface of silver nanoparticles. Naturally, these sensitizers can appear to be effective for Sm<sup>3+</sup> ions. Moreover, the most intense absorption band  ${}^{6}H_{5/2} \longrightarrow {}^{6}P_{3/2} (\lambda \approx 400 \text{ nm})$  for these ions in the visible spectral range [1] is in resonance with the surface plasmon absorption band of  $(Ag^{0})_{n}$  nanoparticles in silica gel glasses. Therefore, in our work, silica gel glasses were chosen as the host matrix. Upon doping of these glasses with samarium and silver, this enabled us to analyze the sensitization of the luminescence of the rare-earth activator by silver ions and the influence of silver nanoparticles on the intensity of optical transitions of the activator under investigation. In addition, we attempted to reveal the specific features of the incorporation of silver into silica gel glasses.

### 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Experimental samples were synthesized from an aerosil (ultrafine SiO<sub>2</sub>) with a grain diameter of ~300 nm by the rapid sol–gel method, which made it possible to prepare thin silica plates (thickness,  $h \le 2$  mm) from an initial solution for a light day. The synthesis process involved the dispersion of the aerosil in an aqueous solution, xerogel formation, drying, and sintering in air at  $T \approx 1240$ °C. The samples were activated by impregnating xerogels with water–alcohol solutions of silver and samarium nitrates at concentrations of 0.01 and 1.00 wt %, respectively. A number of glasses thus synthesized were subsequently heat treated in hydrogen at different temperatures  $T_{ann}$ .

The absorption spectra were recorded on a Cary-500 spectrophotometer and represented in the form of the dependence of the optical density on the wavelength  $\lambda$ . The steady-state luminescence spectra and luminescence excitation spectra were measured on an SFL-1211A spectrofluorimeter and were then corrected for the spectral sensitivity of the recording system and the spectral density distribution of exciting radiation, respectively. These spectra were normalized and represented as the dependence of the number of luminescence or excitation photons per unit range of wavelengths  $dN/d\lambda$  on the wavelength  $\lambda$ .

The luminescence kinetics and instantaneous luminescence spectra were investigated on an automated laser spectrometer upon excitation of the fifth ( $\lambda = 213$  nm) and fourth ( $\lambda = 266$  nm) harmonics of a single-pulse neodymium laser (pulse duration,  $\approx 10$  ns). The radiation under investigation was separated with an MSD-1 grating monochromator and recorded using the photoelectric method with an analog-to-digital converter, followed by the data output to a computer. When recording the instantaneous spectra, the signal was collected for 5  $\mu$ s at different delay times  $t_{del}$  with respect to the exciting pulse. These spectra were also corrected for the spectral sensitivity of the recording system. The minimum time constant of the measuring circuit was approximately equal to 60 ns. All spectral measurements were performed at T = 298 K.

#### **3. EXPERIMENTAL RESULTS**

The absorption spectra of the Ag-, Sm-, and (Sm, Ag)-containing glasses of different thicknesses are shown in Fig. 1. For comparison, this figure also shows the absorption spectrum of the undoped glass (curve 1). It can be seen from Fig. 1 that, at  $\lambda \ge 200$  nm, the spectrum of the Ag-containing glass sintered in air exhibits only a long-wavelength wing of the intense UV band (curve 2). The spectrum of the Sm-containing glass in the same spectral range contains a band with a lower intensity (curve 3). The intensity of the UV absorption band of the coactivated glass (curve 4) is also lower than that of the corresponding band of the Ag-containing glass. Moreover, there are differences in the shape of the profiles of these bands. Annealing of the Ag-containing glass in hydrogen at  $T_{ann} = 950^{\circ}$ C for  $t_{ann} = 30$ min leads to the appearance of the intense narrow band at  $\lambda \sim 400$  nm (curve 5). A similar band with a maximum at  $\lambda \approx 392$  nm also appears in the spectrum of the coactivated glass annealed at  $T_{ann} = 800^{\circ}$ C. However, the intensity of this band is many times lower (curve 6). An increase in the annealing temperature  $T_{ann}$  to 950°C (curve 7) and 1200°C (curve 8) is accompanied by a considerable decrease in the intensity of this band and a long-wavelength shift in its maximum by 5 and 20 nm, respectively.

The steady-state luminescence spectra of the Agand (Sm, Ag)-containing glasses (normalized to the maximum intensities) are shown in Figs. 2a–2c. It can



**Fig. 1.** Absorption spectra of (1) undoped, (2, 5) Ag-, (3) Sm-, and (4, 6–8) (Sm, Ag)-containing glasses (a) sintered in air and (b) additionally annealed in hydrogen.  $T_{ann} = (6)$  800, (5, 7) 950, and (8) 1200°C.  $t_{ann} = 30$  min. h = (5) 0.17, (2–4) 0.30, and (1, 6–8) 0.50 mm.

be seen from this figure that the spectrum of the Agcontaining glass sintered in air at the excitation wavelength  $\lambda_{exc} = 260$  nm (curve 1) exhibits a relatively broad UV band with the maximum at the wavelength  $\lambda \approx 360$  nm and that, in the long-wavelength range of this band, there is a broader band with a lower intensity. In the spectrum of this glass at the excitation wavelength  $\lambda_{\text{exc}} = 220$  nm (curve 2), the relative intensity of the UV band increases, the band is narrowed, and the maximum is insignificantly shifted (by  $\approx 7$  nm) toward the short-wavelength range. In the spectrum of the coactivated glass measured at the excitation wavelength  $\lambda_{\text{exc}} = 260 \text{ nm}$  (curve 3), there arises a series of relatively narrow bands in the yellow-red spectral range due to the transitions from the  ${}^{4}G_{5/2}$  state of Sm<sup>3+</sup> ions [1]. Moreover, the relative intensity of the broad bands characteristic of the Ag-containing glass decreases many times and the UV band is considerably shifted (by  $\approx 10$  nm) toward the short-wavelength range. At the excitation wavelength  $\lambda_{exc} = 220$  nm, this glass luminesces predominantly in the range of the *f*-*f* transitions of Sm<sup>3+</sup> ions and the intensity of the broad bands in the spectrum further decreases (curve 4). The luminescence spectrum of the coactivated glass measured upon direct excitation of the rare-earth activator ( $\lambda_{exc} = 400 \text{ nm}$ ) differs in the shape of the spectral bands and the fraction of photons emitted within these bands (curve 5). It should be noted that this luminescence spectrum differs from the spectrum of the Sm-containing glass upon



**Fig. 2.** Luminescence spectra of (1, 2) Ag- and (3–6) (Sm, Ag)-containing glasses (1–5) sintered in air and (6) annealed in hydrogen.  $\lambda_{\text{exc}} = (2, 4)$  220, (1, 3, 6) 260, and (5) 400 nm.  $\Delta \lambda_{\text{exc}} = 4$  nm.  $\Delta \lambda_{\text{mon}} = 2$  nm.  $T_{\text{ann}} = 950^{\circ}$ C.

identical excitation only in a higher peak intensity (by approximately 30%) of the spectral component at  $\lambda \approx 660$  nm. Annealing in hydrogen ( $T_{ann} = 950^{\circ}$ C) results in the disappearance of the luminescence of the Ag-containing glass but almost does not affect the luminescence spectrum of the Sm-containing glass (these spectra are not shown in Fig. 2). The same annealing of the coactivated glass leads to a multiple increase in the relative intensity of the broad UV band, its substantial long-wavelength shift (by  $\approx 25$  nm), and a noticeable broadening (by a factor of 1.1) in the spectrum at the excitation wavelength  $\lambda_{exc} = 260 \text{ nm}$ (curve 6), as well as to a decrease in the relative intensity of the spectral component at  $\lambda \approx 660$  nm to the intensity characteristic of spectrum 5. At the excitation wavelength  $\lambda_{exc} = 400$  nm, the intensity of luminescence of Sm<sup>3+</sup> ions in the coactivated glass annealed in hydrogen decreases by a factor of approximately 3.5, whereas the intensity of their luminescence and the luminescence spectrum at the excitation wavelength  $\lambda_{\text{exc}} = 220 \text{ nm are almost independent of this annealing.}$ 



**Fig. 3.** Instantaneous luminescence spectra of (a) Ag- and (b) (Sm, Ag)-containing glasses sintered in air.  $\lambda_{\text{exc}} = 266$  nm.  $t_{\text{del}} = (1) 0, (2) 1$ , and (3) 100 µs.

As regards the nonactivated glass, the intensity of its luminescence appears to be lower than that of the Agcontaining glass by at least two orders of magnitude and, therefore, the corresponding luminescence spectrum is not shown.

The instantaneous luminescence spectra of the Agand (Sm, Ag)-containing glasses sintered in air and measured at the excitation wavelength  $\lambda_{exc} = 266$  nm are shown in Fig. 3. It can be seen that, at the delay time  $t_{del} = 0$ , the spectrum of the Al-containing glass (Fig. 3a) involves the intense UV band with a maximum at  $\lambda \approx 320$  nm and a shoulder at  $\lambda \approx 360$  nm, as well as the low-intensity but clearly distinguishable bands at  $\lambda \approx 430$  and 630 nm (curve 1). An increase in the delay time to 1  $\mu$ s (curve 2) and 100  $\mu$ s (curve 3) for this glass is attended initially by the disappearance of the short-wavelength and long-wavelength bands and then by a considerable shift in the barycenter of the remaining UV band (from 365 to 375 nm), the disappearance of traces of the band at  $\lambda \approx 430$  nm, and the appearance of the broad band at  $\lambda \approx 540$  nm. The luminescence spectrum of the coactivated glass (Fig. 3b) at the delay time  $t_{\rm del} = 0$  contains intense bands at  $\lambda \approx 370$  and 500 nm and weaker bands at  $\lambda \approx 320$  and 620 nm (curve 1). In the spectrum at the delay time  $t_{del} = 1 \ \mu s$ , the bands at  $\lambda \approx 320, 500$ , and 620 nm disappear; the barycenter of the intense UV band is shifted toward the short-wavelength range to  $\lambda \approx 360$  nm; and there arises a low-intensity band at  $\lambda \approx 660$  nm (curve 2). An increase in the delay time  $t_{del}$  to 100 µs results in a significant weakening of the UV band and the appearance of the broad band at  $\lambda \approx 550$  nm and intense narrow bands associated with the  $\text{Sm}^{3+}$  ions (curve 3).



**Fig. 4.** Luminescence excitation spectra of (1, 2) Ag-, (3–6) (Sm, Ag)-, and (7) Sm-containing glasses (1–7) sintered in air and (4, 6) annealed in hydrogen.  $T_{ann} = 950^{\circ}$ C.  $t_{ann} = 3$  h.  $\lambda_{mon} = (1, 3, 4)$  360, (2) 520, and (5–7) 650 nm.

Figure 4 shows the steady-state luminescence excitation spectra of the Ag-, (Sm, Ag)-, and Sm-containing glasses. The spectra presented in Fig. 4a are normalized to the maximum luminescence intensity. In Fig. 4b, the spectra are normalized to the intensity of the  ${}^{6}H_{5/2} \longrightarrow$  ${}^{4}I_{9/2}$  band ( $\lambda \approx 485$  nm) of Sm<sup>3+</sup> ions, which lies outside the plasmon absorption band of  $(Ag^0)_n$  nanoparticles. It can be seen from Fig. 4 that, for the Ag-containing glass sintered in air, the broad UV luminescence band (the recording wavelength  $\lambda_{mon} = 360 \text{ nm}$ ) corresponds to a broad band at the wavelength  $\lambda \approx 225$  nm in the luminescence excitation spectrum (curve 1) and the longwavelength luminescence band (the recording wavelength  $\lambda_{mon} = 520$  nm) is associated with bands at the wavelengths  $\lambda \approx 270$  nm and  $\lambda \leq 200$  nm (curve 2). Additional doping of this glass with samarium leads to a substantial long-wavelength shift in the maximum of the excitation band upon recording within the UV luminescence band (curve 3). The annealing of the aforementioned glass in hydrogen results in a narrowing of this band by a factor of approximately two (curve 4). The luminescence excitation spectrum of the coactivated glass at the recording wavelength  $\lambda_{mon} = 650 \text{ nm}$ contains a number of low-intensity relatively narrow bands in the wavelength range 330-500 nm and an intense broad band with the maximum at the wavelength  $\lambda \approx 215$  nm (curve 5). The annealing of this glass in hydrogen results in a substantial decrease in the relative intensity of the narrow bands at  $\lambda < 430$  nm and the long-wavelength wing of the broad UV excitation band (curve 6). In the luminescence excitation spec-



**Fig. 5.** Kinetics of luminescence in (1, 3) Ag- and (2, 4–6) (Sm, Ag)-containing glasses.  $\lambda_{\text{exc}} = (a, 5)$  213 and (b, 6) 266 nm.  $\lambda_{\text{mon}} = (a)$  360, (b) 520, (c) 650 nm.

trum of the Sm-containing glass at the recording wavelength  $\lambda_{mon} = 650$  nm (curve 7), the relative intensities of the narrow bands differ significantly from those of the luminescence excitation spectrum of the coactivated glass and the efficiency of excitation within the broad UV band is many times lower.

The kinetics of luminescence of the Ag- and (Sm, Ag)-containing glasses is illustrated in Fig. 5. It can be seen from this figure that, for the Ag-containing glass, the luminescence decay within the UV band (the recording wavelength is  $\lambda_{mon} = 360$  nm) at the excitation wavelength  $\lambda_{exc} = 213$  nm (Fig. 5a) occurs according to a nonexponential law (curve 1). The mean time  $\bar{\tau}$  of this process outside the rapid initial stage (that cannot be analyzed because its mean time  $\bar{\tau}$  is less than the time constant of the measuring circuit) is approximately equal to 15.6 µs. For the coactivated glass under identical excitation and recording conditions (curve 2), the fraction of photons emitted at the rapid initial stage decreases noticeably and the decay time  $\bar{\tau}$  outside this stage increases insignificantly (to 17.5 µs). Upon

recording of the luminescence within the broad longwavelength band ( $\lambda_{mon} = 520$  nm) at the excitation wavelength  $\lambda_{exc} = 266$  nm (Fig. 5b), the kinetic curves of both glasses also involve the steep initial portions. However, the mean time  $\bar{\tau}$  for this portion in the case of the Ag-containing glass (curve 3) is less than the time constant of the measuring circuit, whereas the mean time for the coactivated glass (curve 4) is  $\bar{\tau} \approx 3.0$ μs (see the inset to Fig. 5b). These glasses also differ substantially in the behavior and the rate of luminescence decay outside the initial portion (the mean times for curves 3 and 4 are  $\bar{\tau} \approx 16$  and 40 µs, respectively). For the coactivated glass upon recording in the range of the *f*-*f* bands of Sm<sup>3+</sup> ions (Fig. 5c,  $\lambda_{mon} = 650$  nm) at the excitation wavelength  $\lambda_{exc} = 213$  nm outside the steep initial portion, the luminescence decays according to an approximately exponential law at a decay time  $\tau \approx 1.64$  ms (curve 5). This decay time coincides with the time constant of the final stage of the luminescence decay in the Sm-containing glass ( $\tau \approx 1.57$  ms) to within the experimental error. At the excitation wavelength  $\lambda_{exc} = 260$  nm (curve 6), the time constant for the final decay stage increases to 2.0 ms and the decay time  $\tau$  for the initial stage increases to 0.014 ms (see the inset to Fig. 5c).

# 4. DISCUSSION OF THE EXPERIMENTAL RESULTS

As is known [9–14], silver can be incorporated into glassy matrices in the form of simple ions Ag<sup>+</sup>, double ions  $(Ag^+)_2$  and  $(Ag_2)^+$ , and more complex ions  $(Ag_n)^{m+}$ . The absorption and luminescence bands of these ions are observed in the UV and visible spectral ranges and can be considerably shifted depending on the composition and structure of glasses. It should be noted that these bands for Ag+ ions are located at the shortest wavelengths. The excited energy levels of these ions are observed at frequencies of 46046 cm<sup>-1</sup> (217.17 nm)  $({}^{1}D_{2})$ , 43739 cm<sup>-1</sup> (228.63 nm)  $({}^{3}D_{1})$ ,  $40741 \text{ cm}^{-1}$  (245.45 nm) (<sup>3</sup>D<sub>2</sub>), and 39163 cm<sup>-1</sup>  $(255.34 \text{ nm}) (^{3}D_{3}) [15, 16]$ . There can also occur a predominant incorporation of silver in the form of isolated atoms [17], which absorb in a relatively narrow band at the wavelength  $\lambda \approx 360$  nm [18], especially at a low concentration of nonbridging oxygen ions in the glass. Under the appropriate conditions, silver ions in the glass, as a rule, are easily reduced with the aggregation into metal nanoparticles characterized by the intense surface plasmon absorption band with the maximum in the wavelength range  $\lambda \approx 390-450$  nm.

According to the above data, the absence of the bands at the wavelengths  $\lambda \approx 360$  and 400 nm in the absorption spectra of the Ag- and (Sm, Ag)-containing glasses sintered in air (Fig. 1, curves 2, 4) allows the assumption that, for the most part, silver is in the ionic form. In this case, the significant change in the profile of the recorded portion of the UV band upon introduc-

tion of silver at identical concentrations into the undoped and samarium-containing glasses indicates that silver optical centers formed in these glasses have different structures. The appearance of the intense plasmon band in the spectrum of the Ag-containing glass annealed in hydrogen (Fig. 1, curve 5) suggests that silver ions are effectively reduced to the atomic state with the formation of metal nanoparticles. The fact that the reduction of silver ions in the coactivated glasses is many times less effective could be associated with the competing effect of samarium ions. However, judging from the absence of the most intense luminescence band  ${}^{5}D_{0} \longrightarrow {}^{7}F_{0} (\lambda \approx 682 \text{ nm})$  of Sm<sup>2+</sup> ions in the luminescence spectrum (Fig. 2, curve 6), the efficiency of the reduction of Sm<sup>3+</sup> ions to the doubly charged state can be treated as negligible. Therefore, it is reasonable to assume that complex optical centers involving samarium and silver ions with the structure that prevents the interaction of hydrogen with these ions are formed in the aforementioned glass. The decrease in the intensity and the long-wavelength shift in the plasmon band of  $(Ag^0)_n$  nanoparticles (formed in small amounts in this glass upon annealing in hydrogen) with an increase in the annealing temperature  $T_{\rm ann}$  (compare curves 6-8 in Fig. 1) indicate that these nanoparticles are sequentially oxidized beginning with small-sized particles. The generation of nonbridging oxygen ions required for this process most likely becomes possible due to the transformation of the local environment of the Sm–Ag centers.

The positions of the excited energy states of isolated Ag<sup>+</sup> ions [15, 16] allow us to assume that the intense UV band in the steady-state luminescence spectrum of the Ag-containing glass (Fig. 2a) is a superposition of bands attributed to the spin-allowed transitions  $4d^95s^1$  $({}^{1}D_{2}) \longrightarrow 4d^{10} ({}^{1}S_{0})$  and the spin-forbidden transitions  $4d^9\bar{5}s^1 ({}^3D_{1-3}) \longrightarrow 4d^{10} ({}^1S_0)$  of these ions. It is evident that the nature of the broad band with a lower intensity in the visible spectral range is more complex. The contribution to this band can be made by double centers  $(Ag_2)^+$ and  $(Ag^+)_2$  ( $\lambda_{max} \approx 450$  and 550 nm, respectively [12]) and triple centers, probably,  $(Ag_3)^{2+}$  ( $\lambda_{max} \approx 600$  nm [11, 13]). According to [14], the intercombination band  $4d^95s^1$  ( $^3D_{1-3}$ )  $\longrightarrow 4d^{10}$  ( $^1S_0$ ) of isolated Ag<sup>+</sup> ions can also lie in this range ( $\lambda_{max} \approx 450$  nm). If the introduction of silver leads to an increase in the concentration of structural defects in the matrix, the contribution to the band under consideration can also be made by oxygendeficient centers and nonbridging oxygen ions ( $\lambda_{max} \approx$ 460 and 670 nm, respectively [19]). However, the contribution of more complex oligometric clusters  $(Ag_n)^{m+}$  $(\lambda \approx 600 \text{ nm})$  can be ignored because of the absence of  $(Ag^{0})_{n}$  nanoparticles stabilizing these clusters [9].

A multiple decrease in the intensity of the luminescence bands of the Ag-containing glass upon doping with samarium suggests that excitations are effectively transferred from simple and complex silver ions to Sm<sup>3+</sup> ions. In this case, the considerable decrease in the relative intensity of the luminescence of Ag<sup>+</sup> ions with

a decrease in the excitation wavelength  $\lambda_{exc}$  from 260 to 220 nm (compare curves 3 and 4 in Fig. 2) allows us to assume that the most effective transfer of excitations to the rare-earth activator occurs through the charge-transfer state  $Sm^{3+} \leftarrow O^{2-}$ , because the matrix elements for the *f*-*f* transitions of Sm<sup>3+</sup> ions at  $\lambda = 200-330$  nm are very small [20]. The shift in the barycenter of the UV luminescence band from 355 to 335 nm (accompanying the above decrease in the intensity) can be associated (if the aforementioned assumption that this band is the superposition of the bands is valid) with the dominant transfer of excitations from the triplet states of Ag<sup>+</sup> ions to Sm<sup>3+</sup> ions. The change observed in the luminescence spectrum of the coactivated glass in the range of the spectral bands  ${}^{5}G_{5/2} \longrightarrow {}^{6}H_{5/2} (\lambda_{max} \approx 565 \text{ nm}),$  ${}^{5}G_{5/2} \longrightarrow {}^{6}H_{7/2} (\lambda_{max} \approx 603 \text{ nm}), \text{ and } {}^{5}G_{5/2} \longrightarrow {}^{6}H_{9/2} (\lambda_{max} \approx 650 \text{ nm}) \text{ of Sm}^{3+} \text{ ions upon changing over from}$ the direct excitation of these ions to the excitation through the sensitizer (compare curve 5 in Fig. 2 with curves 3 and 4) confirms the formation of Sm-Ag centers. It should be noted that the identity of the Sm<sup>3+</sup> luminescence spectra (except for the portion at  $\lambda \approx 660$  nm) for the glasses with and without silver at the excitation wavelength  $\lambda_{exc}$  = 400 nm is reasonable to explain by the small fraction of complex centers due to the small atomic ratio Ag/Sm  $\approx 0.2$ . The formation of Sm–Ag centers is also supported by the short-wavelength shift in the UV luminescence band upon introduction of samarium into the silver-containing glass (compare curves 1 and 3 in Fig. 2). Since the strength of a single chemical bond Sm-O according to calculations using the technique proposed in [21] is substantially lower than that of a Si-O bond (1.25 and 1.54 relative units, respectively), the "displacement" of the oxygen ion from the silver ion toward the counterion in the Sm-O-Ag structural groups should be smaller than that in the Si-O-Ag groups. This should result in an increase in the degree of covalence of the Ag-O bond in the coactivated glass and the long-wavelength shift in the UV luminescence band. The experimentally observed short-wavelength shift allows us to make the inference regarding the decrease in the splitting of the excited states of Ag<sup>+</sup> ions in the Sm–Ag centers.

It is worth noting here that, after annealing in hydrogen, the relative intensity of the component at  $\lambda \approx 660$  nm in the luminescence spectrum of the coactivated glass upon excitation through silver ions decreases to the intensity characteristic of the direct excitation of Sm<sup>3+</sup> ions (Fig. 2c). When this components is considered a superposition of the corresponding Stark band associated with the  ${}^{5}G_{5/2} \longrightarrow {}^{6}H_{9/2}$  transition in Sm<sup>3+</sup> ions and the luminescence band of nonbridging oxygen centers [19], the decrease in the intensity of this band can be explained by the disappearance of these centers due to the interaction with hydrogen with the formation of structurally bound hydroxyl ions. By developing this idea, we can assume that the formation of Sm-Ag centers is attended by the generation of nonbridging oxygen ions, which in the course of annealing of the glass in  $H_2$  bind hydrogen atoms, thus preventing the reduction of silver ions. In this case, judging from a substantial change in the luminescence spectrum of silver ions (compare curves 3 and 6 in Fig. 2), the structure of their environment in the Sm–Ag centers undergoes a transformation. Moreover, the intensity and the shape of the broad UV band of this glass saturated with hydrogen depend on the duration and intensity of excitation, which indicates the formation of a photochromic phase. However, the analysis of this fact is beyond the scope of the present paper.

The short-lived intense UV luminescence band at  $\lambda_{max}\approx 320$  nm in the instantaneous luminescence spectrum ( $t_{del} = 0 \ \mu s$ ) of the Ag-containing glass (Fig. 3a, curve 1) can be assigned with certainty to the  $4d^95s^1$  $({}^{1}D_{2}) \longrightarrow 4d^{10} ({}^{1}S_{0})$  transitions in isolated Ag<sup>+</sup> ions. In this case, the shoulder at  $\lambda \approx 360$  nm in the luminescence spectrum is associated with the  $4d^95s^1$  $({}^{3}D_{1-3}) \longrightarrow 4d^{10} ({}^{1}S_{0})$  transitions in these ions and the low-intensity luminescence bands at  $\lambda \approx 430$  and 630 nm are most likely attributed to the  $4d^{10}5p \longrightarrow 4d^{10}5s$  transitions in  $(Ag_2)^+$  centers ( $\tau \le 10$  ns [12]) and  $(Ag_3)^{2+}$  trimers ( $\tau \le 25$  ns [13]). The contribution to the spectrum under consideration from the oxygen-deficient centers (in the matrix) considered in the discussion of Fig. 2 can be disregarded, because their singlet-singlet band is located at shorter wavelengths ( $\lambda \approx 285 \text{ nm}$  [19]), and the contribution from the triplet-singlet transitions in these centers and nonbridging oxygen centers can be ignored because of the long decay times  $\bar{\tau}$  (~10 ms and 10 µs, respectively [19]). The observed long-wavelength shift in the intercombination luminescence band of isolated Ag<sup>+</sup> ions with an increase in the delay time  $t_{del}$  (compare curves 2 and 3 in Fig. 3a) suggests their rather inhomogeneous local environment and migration of excitations toward the centers with the lowest position of the metastable state. The increase in the relative intensity of the band at  $\lambda \approx 540$  nm indicates that the  $(Ag^{+})_{2}$  centers have a long decay time  $\bar{\tau}$ .

The radical change in the instantaneous luminescence spectra upon coactivation of the glass under consideration with Sm<sup>3+</sup> ions (Fig. 3b) offers additional arguments in support of the formation of Sm-Ag centers. Actually, the redistribution of the relative intensity of the Ag<sup>+</sup> luminescence in favor of the intercombination transition (compare curves 1 in Figs. 3a and 3b) suggests that these transitions are promoted by heavy atoms, which is possible upon formation of Ag-O-Sm bonds. In turn, the absence of the long-wavelength shift in the  $4d^95s^1$   $(^3D_{1-3}) \longrightarrow 4d^{10}$   $(^1S_0)$  band with an increase in the delay time  $t_{del}$  from 1 to 100 µs (compare curves 2 and 3 in Fig. 3b) indicates that the local environment of Ag+ ions becomes considerably more homogeneous. This can also be associated with the formation of Sm-Ag centers. The blue shift in the shortlived long-wavelength band (compare the "tails" of curves 1 in Figs. 3a and 3b) allows us to make the inference that the Sm–Ag centers can involve not only simple silver ions but also complex silver ions, in the given case,  $(Ag_3)^{2+}$ . In regard to the short-lived broad luminescence band at  $\lambda \approx 500$  nm (Fig. 3b, curve 1), it is reasonable to attribute this band to the formation of Sm– $(Ag_3)^{2+}$  centers. The band that manifests itself for the delay time  $t_{del} = 1 \ \mu$ s at  $\lambda \approx 660$  nm (Fig. 3b, curve 2) can be assigned to the nonbridging oxygen centers. The absence of the band at the wavelength  $\lambda \approx 660$  nm in the instantaneous luminescence spectrum of the Ag-containing glass is a weighty argument in support of the assumption (made in the discussion of the data presented in Fig. 2) that oxygen is generated upon the formation of Sm–Ag centers.

The substantial change in the shape and position of the barycenter of the luminescence excitation band of the Ag<sup>+</sup> centers upon introduction of samarium (compare curves 1 and 3 in Fig. 4) confirms the inference about the formation of Sm-Ag centers. In turn, the narrowing of this band after annealing of the coactivated glass in hydrogen (compare curves 3 and 4 in Fig. 4) supports the transformation of the local environment of silver ions in these centers. The UV luminescence excitation band at  $\lambda \sim 230$  nm in the spectrum of the Smcontaining glass (Fig. 4, curve 7) can be attributed to the  $O^{2-} \longrightarrow Sm^{3+}$  charge-transfer band. The multiple increase in the intensity and width of the Sm<sup>3+</sup> luminescence excitation band in this UV spectral range for the coactivated glass (Fig. 4, curve 5) confirms the inference made when analyzing Fig. 2 that excitations are effectively transferred from silver ions to samarium ions. It is easy to estimate that this sensitization for the coactivated glass makes it possible to increase the effectiveness of the use of UV radiation at  $\lambda < 300$  nm by a factor of approximately 30 for the excitation of the Sm<sup>3+</sup> luminescence. It should be noted that the noticeable increase in the relative intensity of the  ${}^{6}H_{5/2} \longrightarrow$  ${}^{6}P_{3/2}$  band is one more argument in favor of the formation of Sm-Ag centers. The significant decrease in the intensity of this band and the f-f bands at shorter wavelengths after annealing of the coactivated glass in hydrogen indicates the effective quenching of the Sm<sup>3+</sup> luminescence through the transfer of excitations to  $(Ag^{0})_{n}$  nanoparticles from states with frequencies that are resonant or higher than the frequency of the surface plasmon absorption band. The absence of the decrease in the intensity of the short-wavelength wing of the broad UV luminescence excitation band of Sm<sup>3+</sup> ions after the same annealing (compare curves 5 and 6 in Fig. 4) allows us to make the inference that the  $Sm^{3+}$ -Ag<sup>+</sup> centers are located far from  $(Ag^0)_n$  nanoparticles. It is clear that nanoparticles are formed predominantly with the participation of complex silver ions contained in the Sm-Ag centers. This ensures a more effective dissipation of excitations of Sm<sup>3+</sup> ions in these centers.

The presence of the steep initial portions in the kinetic curves of luminescence decay within the UV band of the Ag- and (Sm, Ag)-containing glasses at the excitation wavelength  $\lambda_{exc} = 213$  nm (Fig. 5a) can be

explained by the overlap of the spin-allowed band  $4d^95s^1$  ( $^1D_2$ )  $\longrightarrow$   $4d^{10}$  ( $^1S_0$ ) with the recording range  $(\lambda_{mon} = 360 \text{ nm})$ . A rather large value of  $\bar{\tau}$  ( $\approx 16-18 \text{ } \mu s$ ) for the UV luminescence band under consideration outside the steep initial portion indicates that the parityand spin-forbidden transitions  $4d^95s^1 ({}^3D_{1-3}) \longrightarrow 4d^{10}$  $({}^{1}S_{0})$  contribute to this band. An insignificant deviation from the exponential behavior of the luminescence decay in both glasses at the middle stage suggests a weak deactivation of Ag<sup>+</sup> ions through the transfer of excitations to a disordered ensemble of acceptors. A nearly constant decay time  $\bar{\tau}$  for this band after introduction of samarium into the glass (compare curves 1 and 2 in Fig. 5a) at a more than thirtyfold decrease in its integrated intensity is possible only for the exchange mechanism of the excitation transfer from Ag<sup>+</sup> ions to Sm<sup>3+</sup> ions when, owing to the strong interaction, the Ag<sup>+</sup> luminescence in the Sm-Ag centers is absent and we observe only the luminescence of individual Ag+ ions. The occurrence of this interaction is an additional evidence of the formation of Sm<sup>3+</sup>–Ag<sup>+</sup> centers.

The steep initial portion in the kinetic curve of luminescence decay in the Ag-containing glass at the excitation wavelength  $\lambda_{exc} = 266$  nm and the recording wavelength  $\lambda_{mon} = 520$  nm (Fig. 5b, curve 3) can be attributed to the  $4d^{10}5p \longrightarrow 4d^{10}5s$  transitions in  $(Ag_2)^+$ centers characterized by a decay time  $\bar{\tau} < 10$  ns [12], whereas the other portion of the kinetic curve most likely describes the luminescence of  $(Ag^+)_2$  centers. A substantial increase in the decay time  $\bar{\tau}$  in the range under consideration, together with a decrease in the luminescence intensity, upon introduction of samarium into the glass (compare curves 3 and 4 in Fig. 5b) confirms the inference made in the analysis of Fig. 3 that the Sm-Ag centers are formed with the participation not only of simple silver ions but also of complex silver ions. This fact can also be treated as evidence of an increase in the symmetry of these centers. Apparently, the complex silver ions can be represented by both silver dimers and silver trimers. Indeed, the formation of  $Sm^{3+}-(Ag_3)^{2+}$  centers can be supported by the blue shift in the short-lived bands at  $\lambda \approx 640$  nm, which is observed in the instantaneous luminescence spectra (compare curves 1 in Fig. 3). With due regard for the fast luminescence of  $(Ag_3)^{2+}$  ions ( $\bar{\tau} \leq 25$  ns [13]) and, evidently, a lower position of their metastable level as compared to the  ${}^4G_{5/2}$  level, the sensitization of the luminescence of the rare-earth activator in the Sm<sup>3+</sup>- $(Ag_3)^{2+}$  centers seems to be highly improbable. More likely, there occurs a reverse transfer of excitations from  $Sm^{3+}$  ions to  $(Ag_3)^{2+}$  ions. Apparently, it is this transfer that explains the increase in the intensity of luminescence of the coactivated glass at 620 nm upon excitation through the sensitizer (compare curves 3 and 5 in Fig. 2).



Fig. 6. Simplified diagram of energy states and channels of excitation transformations in  $Sm^{3+}-Ag^+$  centers.

The luminescence decay in the coactivated glass in the range of the f-f bands of Sm<sup>3+</sup> ions is also a complex process. The rapid initial stage of this process at the excitation wavelength  $\lambda_{exc} = 213$  nm (Fig. 5c, curve 5) can be associated with the fact that the band of the luminescence from the excited state of the charge-transfer complex O<sup>2-</sup>Sm<sup>3+</sup> (this band for the Sm-containing aerosil glass is characterized by  $\lambda_{max} \approx 650$  nm and  $\Delta\lambda \approx 150$  nm) and tails of the luminescence bands of  $(Ag_3)^{2+}$  centers and nonbridging oxygen centers overlap with the recording range. An increase in the luminescence time at this stage for the excitation wavelength  $\lambda_{\text{exc}} = 266 \text{ nm}$  (Fig. 5c, curve 6) to the luminescence time  $\tau \approx 14 \ \mu s$  characteristic of nonbridging oxygen centers [19] is an additional argument in favor of their generation upon formation of Sm–Ag centers. An almost exponential luminescence decay outside the steep initial portion at both excitation wavelengths  $\lambda_{exc}$ is one more confirmation of a high homogeneity of Sm-Ag centers and suggests a weak cross-relaxation quenching of the Sm<sup>3+</sup> luminescence for the used concentrations. In this case, a noticeable difference between the decay times  $\tau(1.5, 2.0 \text{ ms})$  indicates that there are two ensembles of centers, in one of which simple silver ions are energy donors, whereas in the other ensemble (with the longer decay time  $\bar{\tau}$ ) complex silver ions serve as energy donors.

The above results allow us to propose the diagram of energy states and optical transitions for the Sm<sup>3+</sup>-Ag<sup>+</sup> centers (Fig. 6). According to this diagram, upon excitation of Ag<sup>+</sup> ions within the  ${}^{1}S_{0} \rightarrow {}^{1}D_{2}$  transition, a number of absorbed photons are emitted back to the ground state (straight lines) and nonradiatively transferred (dashed lines) to the charge-transfer excited state (CTES) of the O<sup>2-</sup>Sm<sup>3+</sup> complex. The other photons relax to the triplet levels  ${}^{3}D_{1-3}$  (wavy lines). The deactivation of these levels occurs through both the radiative transitions and nonradiative energy transfer to the  $O^{2-}Sm^{3+}$  complexes and/or directly to the corresponding excited states of the  $Sm^{3+}$  ions. The deactivation of the charge-transfer excited state proceeds predominantly via the intramolecular energy transfer to the  $Sm^{3+}$  ions. It seems likely that the deactivation channels through radiative transitions to the charge-transfer ground state (CTGS) and nonradiative energy transfer to the lower triplet state of the Ag<sup>+</sup> ions are not ruled out (also shown in the figure).

#### 5. CONCLUSIONS

Thus, it has been demonstrated that the sintering of silver-doped silica gel glasses in air leads to the formation of simple and complex silver optical centers, which represent  $Ag^+$  isolated,  $(Ag^+)_2$  and  $(Ag_2)^+$  double, and  $(Ag_3)^{2+}$  triple ions with characteristic luminescence spectra. The annealing of these glasses in hydrogen is accompanied by the effective reduction of silver ions and the formation of silver metal nanoparticles. The coactivation of these glasses by Sm<sup>3+</sup> ions results in the formation of complex centers in which the rare-earth activator is bonded to simple and/or complex silver ions through bridging oxygen. This provides an effective intracenter sensitization of the Sm<sup>3+</sup> luminescence by simple and double silver ions according to the exchange mechanism for, at least, Sm<sup>3+</sup>–Ag<sup>+</sup> centers. The formation of Sm-Ag centers is attended by an increase in the concentration of nonbridging oxygen ions, which upon annealing in H<sub>2</sub> bind hydrogen atoms and radically decrease the efficiency of reduction of silver ions. This reduction occurs only in Sm-Ag centers involving complex silver ions, and the  $(Ag^0)_n$  nanoparticles formed are effective quenchers of the excited states of Sm<sup>3+</sup> ions with frequencies that are resonant or higher than the frequency of the surface plasmon absorption band.

#### REFERENCES

- G. E. Malashkevich, I. M. Mel'ni-chenko, E. N. Poddenezhnyĭ, and A. V. Semchenko, Fiz. Tverd. Tela (St. Petersburg) **40** (3), 458 (1998) [Phys. Solid State **40** (3), 420 (1998)].
- I. F. Burmistrov, I. A. Zhmyreva, A. A. Kalenov, V. P. Kolobkov, V. T. Kornev, and P. I. Kudryashov, Zh. Prikl. Spektrosk. **10** (1), 73 (1969) [J. Appl. Spectrosc. **10** (1), 51 (1969)].
- M. C. Farries, P. R. Morkel, and J. F. Townsed, Proc. SPIE—Int. Soc. Opt. Eng. 1171, 271 (1990).
- G. J. Park, T. Hayakawa, and M. Nogami, J. Lumin. 106, 103 (2004).
- V. V. Klimov, M. Ducloy, and V. S. Letokhov, Kvantovaya Élektron. (Moscow) **31** (7), 569 (2001) [Quantum Electron. **31** (7), 569 (2001)].
- 6. H. Lu and J. Ballato, Phys. Chem. Glasses 47, 96 (2006).
- A. C. Marques and R. M. Almeida, J. Non-Cryst. Solids 353, 2613 (2007).

- G. E. Malashkevich, G. P. Shevchenko, S. V. Serezhkina, G. A. Denisenko, and P. P. Pershukevich, Izv. Akad. Nauk, Ser. Fiz. **70**, 1662 (2006).
- G. E. Malashkevich, G. P. Shevchenko, S. V. Serezhkina, P. P. Pershukevich, G. I. Semkova, and G. K. Glushonok, Fiz. Tverd. Tela (St. Petersburg) 49, 1804 (2007) [Phys. Solid State 49 (10), 1891 (2007)].
- E. G. Bondarenko, V. O. Kabanov, G. O. Karapetyan, and O. V. Yanush, Zh. Prikl. Spektrosk. **35** (1), 60 (1981) [J. Appl. Spectrosc. **35** (1), 744 (1981)].
- J. C. Pivin, G. Roger, M. A. Garcia, F. Singh, and D. K. Avasthi, Nucl. Instrum. Methods Phys. Res., Sect. B 215, 373 (2004).
- I. Belharouak, F. Weill, C. Parent, G. Le Flem, and B. Moine, J. Non-Cryst. Solids 293–295, 649 (2001).
- E. Borsella, E. Cattaruzza, G. De Marchi, F. Gonella, G. Mattei, P. Mazzoldi, A. Quaranta, G. Battaglin, and R. Polloni, J. Non-Cryst. Solids 245, 122 (1999).
- E. Borsella, G. Battaglin, M. A. Garcia, F. Gonella, P. Mazzoldi, R. Polloni, and A. Quaranta, Appl. Phys. A: Mater. Sci. Process. **71**, 125 (2000).

- 15. H. Bach, F. G. K. Baucke, and J. A. Duffy, Phys. Chem. Glasses 27, 215 (1986).
- E. Borsella, F. Gonella, P. Mazzoldi, A. Quaranta, G. Battaglin, and R. Polloni, Chem. Phys. Lett. 284, 429 (1998).
- M. A. Garcia, M. Garcia-Heras, E. Cano, J. M. Bastidas, M. A. Villegas, E. Montero, J. Llopis, C. Sada, G. De Marchi, G. Battaglin, and P. Mazzoldi, J. Appl. Phys. 96, 3737 (2004).
- J. Zhang, W. Dong, L. Qiao, J. Li, J. Zheng, and J. Sheng, J. Cryst. Growth **305**, 278 (2007).
- A. N. Trukhin, M. Goldberg, J. Jansons, H.-J. Fitting, and I. A. Tale, J. Non-Cryst. Solids 223, 114 (1998).
- 20. W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. 49, 4424 (1968).
- G. E. Malashkevich, E. N. Poddenezhny, I. M. Melnichenko, and A. A. Boiko, J. Non-Cryst. Solids 188, 107 (1995).

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