Structure and Spectral-Luminescent Properties of Silica Gel-Glasses Containing $CeO_2-Ln_2O_3$ Nanoparticles: Influence of Local Charge Compensator

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Abstract

Silica glasses activated with $CeO_2-Ln_2O_3$ nanocrystallites where Ln ≡ Nd, Sm, Eu, Er have been synthesized by a direct sol–gel–glass transition and their investigation with help of an X-ray diffraction, small-angle neutron scattering, and spectral-luminescent methods carried out. It is established that co-doping of the glasses with magnesium for local charge compensation leads both to significant increase of the nanocrystallites concentration and limitation of their sizes.

1. Introduction

It is the well-known fact that additives of rare earth ions into silica glasses are accompanied normally with their remarkable segregation. Very likely, the Ce^{4+} ions can fall out from this rule thanks to a small ion radius that permits them to fulfill the role of buffer elements facilitating the entry of more volumetric Ln^{3+} ions into the host matrix. For example, the concentration of Ce^{4+} and Ce^{3+} ions in silica glass obtained by the sol–gel methods can significantly exceed 1×10^{20} cm^{-3} without observable worsening optical properties of the glass [1]. In our recent paper [2], we showed that co-doping Ce-containing glasses with Eu^{3+} ions leads to formation of $CeO_2-Eu_2O_3$ nanocrystallites. These latter are characterized by cubic symmetry of Eu(III) oxo complexes, by a weak vibronic interaction of their Eu^{3+} ions with the matrix, and by effective sensitization of the ions luminescence by labile

photoreduced $(Ce^{4+})^-$ ions. The formation of such optical centers permits to impart to silica glasses by unique spectral-luminescent properties. In the present paper, we describe submicroscopic structure and the properties of silica gel-glasses activated with $CeO_2-Ln_2O_3$ nanocrystallites (Ln = Nd, Sm, Eu, Er) in the presence of local charge compensator.

2. Materials and experimental procedure

The glasses were prepared by the direct sol–gel method [1]. Their doping was carried out by impregnating the xerogels with water-alcohol solution of the chloride salts of the corresponding dopants at the concentrations of $C_{Ce} = 1.7$ wt % and $C_{Ln} = 0.6$ wt %. Magnesium with $C_{Mg} = 0.1$ wt % has been used as charge compensator. All the reagents were of grades no poorer than "chemically pure". The vitrification of the activated xerogels with formation of a transparent glasses were carried out in oxygen current to attain a maximum concentration of quadruply charged ions of cerium and removal of $CeO_2-Ce_2O_3$ clusters exhibiting absorption in visible region of the spectrum [3].

The spectra of steady-state luminescence were detected on a spectrofluorimeter (SDL-2) at the room temperature. These spectra were corrected [1], normalized (by reducing their maxima to unity) and represented in the form of the dependence of the number of photons per unit range of wavelengths $dN/d\lambda$ on the wavelength λ or per unit range of wavenumber $dN/d\nu$ on the wavenumber ν.

The presence of crystalline phases in glasses was controlled on a DRON-2.0 x-ray diffractometer ($\lambda = 1.54184$ nm). The microstructure and nanostructure of the glasses was examined using small-angle neutron scattering (SANS) diffractometer D11 installed on the high-flux nuclear reactor of Laue-Langevin Institute (Grenoble) covering q-range from 0.01 to 0.3 $Å^{-1}$ where $q \equiv 4\pi\sin\theta/\lambda$ is scattering vector [4].

3. Results and discussions

Fig. 1 shows the x-ray diffraction patterns of Ce–Eu-containing glasses without (Fig. 1 a) and with Mg (Fig. 1 b) at the same thickness for both glasses. As is seen, the co-doping with Mg leads to evident increase of the Bragg reflections at the angles $2\theta \approx 28°$, 33°, 47°, and 56° which, according to the date of available in the JCPDS-1998 Powder Diffraction File, belong to the CeO_2 cubic lattice with space group of symmetry $O_h^5 - Fm3m$. Similar influence of Mg is preserved at substitution of Eu on

another lanthanides. This fact permits us to conclude that the charge compensator promotes the increase of the $CeO_2-Ln_2O_3$ nanocrystallites concentration.

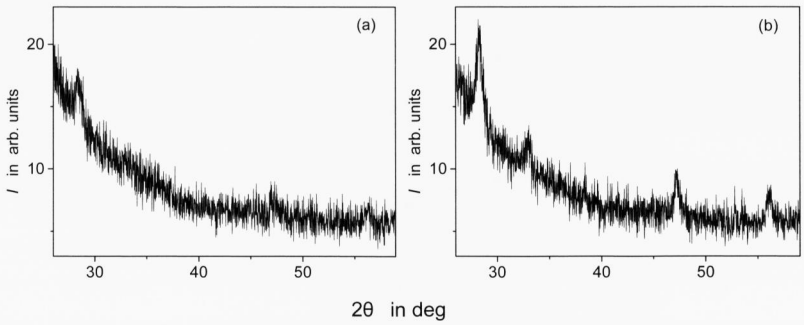

Fig. 1. X-ray diffraction patterns of the (a) Ce–Eu- and (b) Ce–Eu–Mg-containing glasses.

Fig. 2 shows the SANS curves for the Ce–Eu- (curve *1*) and Ce–Eu–Mg-containing (curve *2*) glasses. SANS curves firmly support existence of inhomogeneous structure in both glasses. At the same time there are remarkable differences between them at low q values pointing out on remarkable difference of dimension of inhomogeneities. Determining the gyration radius of inhomogeneities $R_g \equiv \sqrt{-3\Delta \ln I / \Delta q^2}$ [5] from the slope of linear portion of the Guinier plot $\ln I(q^2)$ marked in the Fig. 2 by tangents, we receive its value equal to 410 Å for curve *2* and 775 Å for curve *1*. Proposing spherical form, the diameter of particles $D \equiv R_g \sqrt{20/3}$ is about 1000 and 2000 Å for curves *2* and *1* respectively. The decrease of dimensions of inhomogeneities in two times testifies that the presence of the local charge compensator limits growth of the $CeO_2-Ln_2O_3$ nanoparticles (nanocrystallites) and can lead to increase of uniformity of the glass.

Fig. 3 shows the luminescence spectra of silica glasses activated with $CeO_2-Ln_2O_3$ nanocrystallites where Ln ≡ Eu- (a), Nd- (b), Er (c), Sm- (d), and co-doped with Mg at excitation through the $(Ce^{4+})^-$ (curves *1*). Here, for comparison, the spectra of corresponding Ln-containing glasses at excitation in *f*–*f*-transition of the Ln^{3+} ions (curves *2*) displayed too. The displayed spectrum for the Ce–Eu–Mg-containing

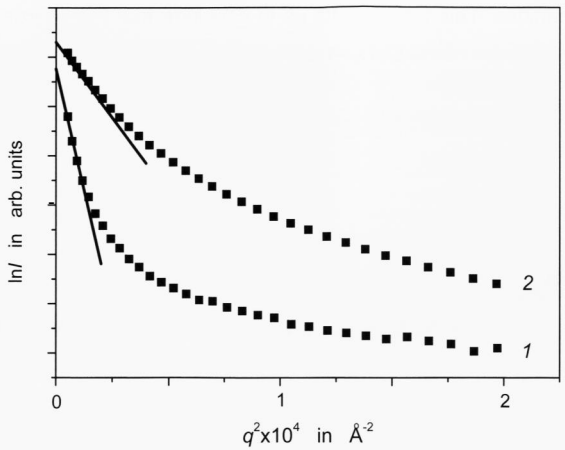

Fig. 2. Dependences of the small-angle neutron scattering intensity on the scattering vector for (*1*) Ce–Eu- and (*2*) Ce–Eu–Mg-containing glasses.

glass is similar to spectrum of Ce–Eu-containing glass which shown in [2] at the same excitation. It was established in [6] that such spectrum is attributed to Eu(III) with cubic symmetry and coordination number of the cation equal to 8. Therefore, the observed similarity leads us to conclusion about identical structure of optical centers for the both glasses. It should be noted that the integrated luminescence intensity at $\lambda_{exc} < 400$ nm for the Ce–Eu–Mg-containing glass is approximately four times higher than for the glass without Mg. Moreover, the first glass at excitation in the $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+} ions (curve *3*) a great extent preserves the characteristic features of the nanocrystallites as distinct from spectrum of the second glass [2, 6]. These facts confirm the conclusion about increase of share of CeO_2–Eu_2O_3 nanocrystallites at doping glass with the local charge compensator that has been done analyzing data of Fig. 1. The absence in the spectrum *1a* of the long-wavelength 'wing' of Ce^{3+} ions luminescence band typical for Ce–Eu-containing glass vitrified in air [2] is explained by significantly smaller concentration of residual Ce^{3+} at vitrified in oxygen. The analysis of spectra of other Ce–Ln–Mg-containing glasses (see curves *1b*, *c*, *d*) testifies that in all cases they have characteristics typical for crystalline phase. It doing so, the major redistribution of the relative luminescence intensity for the Ce–Sm-containing glass (cf. curves 1 *d* and 2 *d*) in favor of bands corresponding to the resolved magnetic dipole transitions

$^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6F_{3/2}$, $^6F_{7/2}$ of Sm^{3+} ions ($\nu \approx 17670$, 16500, 10640, 9390 cm^{-1} respectively) confirms the conclusion about high symmetry of the Ln(III) in the nanocrystallites.

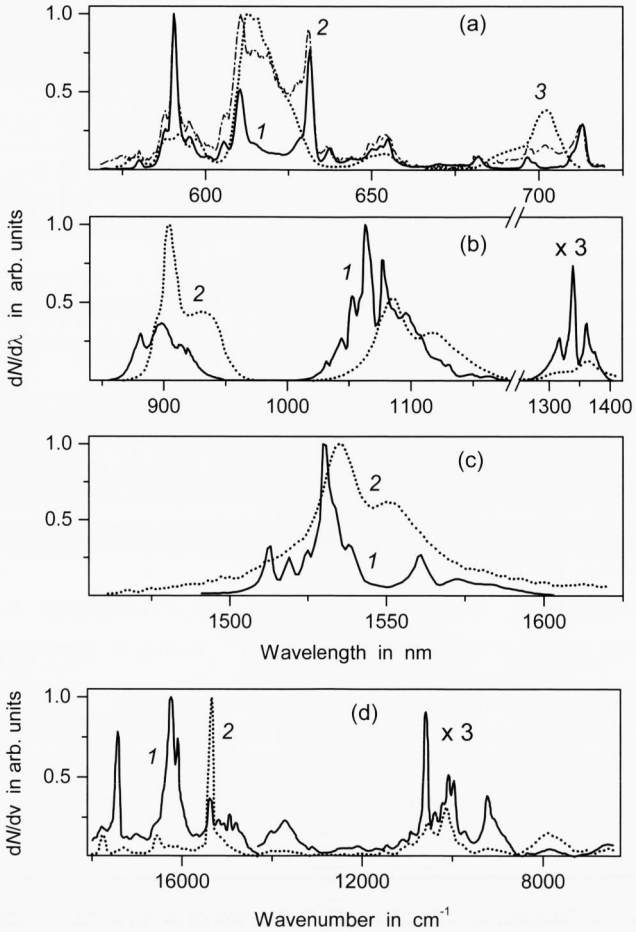

Fig. 3. Luminescence spectra of (*1*, *3*) Ce–Ln–Mg- and (*2*) Ce–Ln-containing glasses where Ln = (a) Eu, (b) Nd, (c) Er, (d) Sm. λ_{exc} = (*1*) 325 nm, (*2*a, *3*) 395 nm, (*2*b) 580 nm, (*2*c) 520 nm, (*2*d) 400 nm.

4. Conclusion

The co-activation of Ce^{4+}-containing silica gel-glasses with Ln^{3+} ions leads to formation of CeO_2–Ln_2O_3 nanocrystallites which impart to the glasses spectral-luminescent properties similar to ones of crystalline phase with a high symmetry of Ln(III) oxo complexes. The co-doping the glasses with a local charge compensator are accompanied by considerable increase of the nanocrystallites concentration and by limitation of their sizes. Such significant influence of the compensator can be useful for creation of new nano-structured glasses.

Acknowledgements

We are grateful to Charles Dewurst (Laue Langevin Institute Grenoble-France) for his assistance in performing the SANS measurements.

This work was supported by the "Science for Peace" NATO program (grant no. SfP 977980) and joint Programme of Belarusian and Russian Foundation for Basic Research (grants no. Ph04R-038 and 04-03-81020, respectively).

References

[1] Malashkevich, G.E.; Poddenezhny, E.N.; Melnichenko, I.M. et al.: Optical centers of cerium in silica glasses obtained by the sol-gel process. J. Non-Cryst. Solids **188** (1995), p. 107-117.

[2] Malashkevich, G.E.; Semkova, G.I.; Sigaev, V.N.; Champagnon, B.: Nano-crystalline nature of high-symmetry Ce^{4+}–Eu^{3+} centers in silica gel-glasses. Phys. Solid State **46** (2004) no. 3, p. 552-556.

[3] Malashkevich, G.E.; Semkova, G.I; Strek W.: Influence of preparation redox conditions and composition of Ce-containing silica gel-glass on its absorption spectrum in the visible region. J. Non-Cryst. Solids **341** (2002), p. 244-246.

[4] Ibel, K.: The neutron Small-Angle Camera D11 at the High-Flux Reactor. Grenoble. J. Appl. Crystallogr. **9** (1976) no. 4, p. 296-300.

[5] Guinier, A; Fournet, G.: Small-Angle Scattering of X-rays. New York: Wiley, 1955.

[6] Malashkevich, G.E.; Makhanek, A.G.; Semchenko, A.V. et al.: Luminescence-spectral properties and structure of optical centers in Eu- and Ce–Eu-containing quartz gel-glasses. Phys. Solid State **41** (1999) no. 2, p. 202-207.