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Spectral and Kinetic Non-Equivalent Site Distribution of Ce^{3+} and Eu^{2+} Ions in Borosilicate Glasses

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Aluminoborosilicate glasses doped by cerium or europium ions were synthesized by high-temperature melting in air and investigated by means of luminescence spectroscopy. Dependence of Ce^{3+} and Eu^{2+} luminescence spectra on experimental conditions (emission or excitation wavelength, registration moment, and excitation regime) was observed. Luminescence decay curves revealed clearly non-exponential behavior and evolution with registration wavelength. The phenomena observed are supposed due to existence the set of distinguishable non-equivalent local cation sites in aluminoborosilicate glasses detected under different experimental conditions for glass properties analyzing.

Keywords: RE ions, luminescence, emission and excitation spectra, kinetic decay.

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1. Introduction

Exploration of rare-earth's (RE) optical properties in different matrices is still remaining one of the interesting scientific tasks during more than half of the century. *E.g.*, the search of the new RE-doped materials with controlled or tuned emission is of great importance for many technological applications and, in particular, for fiber optics and telecommunications [1] and optical electronics [2,3]. It looks especially promising for white-light emission diodes (WLED) engineering which is considered as the next generation of lighting sources in the coming future or tunable lasers [3–6]. In spite of common approaches to produce white light by the combination of blue or ultra-violet (UV) chips and one or more phosphors [7,8], alternatively, a single material with continuous tunable emission under varying light excitation is expected to be a great potential, *i. e.*, multichromatic emission phosphor. By that reason, the design of luminescent materials with widely and continuously tunable excitation and emission is still a challenge in the field of advanced optical application.

It is known that tunable emission in glasses doped with transition ions is wider and more continuous than that in crystalline compounds [6,9,10]. These materials are preferable due to easy fabrication process and ability to absorb sufficient quantity of RE dopants as well as to contain different RE sites in the glass structure. The last phenomenon allows managing certain properties of RE-doped glasses by adjusting, *e.g.*, the glass compositions, activator concentration, or experiment conditions. Although the glass structure can accommodate a lot of RE environments due to its aperiodicity, information about observation of RE sites non-equivalency in glasses is limited. However, during the last decade the reports began to arise offering the possibility to observe the local site environment available for RE ions in glasses using the steady-state luminescence spectroscopy [11–13]. Indeed, observing intense tunable emission simply by changing excitation wavelength and adjusting the concentration of Ce^{3+} [12] and Eu^{2+} ions [6] reveals that there are abundant and distinguishable local RE sites in aluminoborosilicate (ABS) as well as in $SiO_2-Li_2O-SrO-Al_2O_3-K_2O-P_2O_5$ (SLSAKP) glasses. But it should be mentioned that Eu^{2+}/Ce^{3+} spectral non-equivalence could as well result in kinetic non-equivalence entailing the luminescence decay behavior as it was reported for silicate glasses [13]. In the present paper, we report ABS glasses containing Ce^{3+} and Eu^{2+} activator ions and versatility of RE sites, and consider the relation between sites and luminescence decay behavior of the glass studied.

2. Materials and methods

2.1. Synthesis

Two samples of ABS glasses (59.13% SiO_2, 6.38% AL_2O_3, 18.24% B_2O_3, 12.82% Na_2O, 3.5% ZrO_2, in wt%) containing nominally 0.5 wt% of CeO_2 or Eu_2O_3 were prepared by high-temperature melting in air. The dried powders mixture was first heated at 750°C in a Pt crucible during 10 h, then melted at 1500°C for 1 h, and quenched in air. Following the annealing at 500°C during a few hours to release strains, both glass samples were cut into slices of equal thickness. The slices were polished on a hand-grinding wheel with a silicon carbide abrasive with the average grain size of 10 μm (100 grit) to achieve the

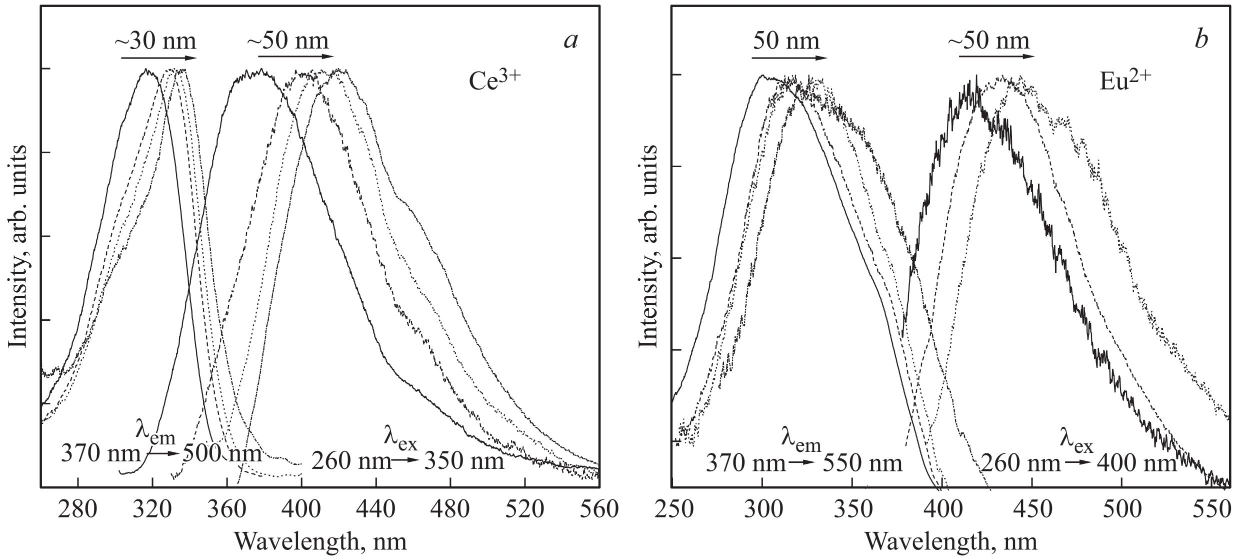

Figure 1. Luminescence and luminescence excitation spectra in ABS glass of *a*) Ce^{3+} ions and *b*) Eu^{2+} ions.

thickness of 0.56 ± 0.05 mm. Each glass was analyzed by X-ray diffraction, which confirmed the amorphous nature of the glass.

2.2. Characterization

The luminescence and excitation spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer with Xe lamp (wavelength from 200 to 900 nm, 1 nm resolution). Time-resolved luminescence experiments were performed to reveal the time dependence of the emission decay. The samples were excited with 266 and 355 nm of an INDI Nd^{3+}:YAG laser (Spectra Physics), which delivers 8 ns pulses at a 10 Hz repetition rate. The pulse energy on the sample was 2 mJ/pulse. The collected light was analyzed by a SHAMROCK spectrograph (focal distance $F = 303$ mm; 150 lines/mm grating and a 400 μm slit, 0.1 nm resolution) combined with an ANDOR Istar intensified charge-coupled device. About a thousand spectra were accumulated at each time step of 1 ns/0.1 μs and a time delay of 200 ns with a 35 ns/1 μs gate width to obtain the evolution of Ce/Eu luminescence lifetime. All measurements were done at room temperature.

3. Results and discussion

The specificity of the glassy matrix consists in the continuous change in the parameters of the RE ions nearest environment under the transition from center to center, which leads to the formation of a continuum of RE centers with different spectral characteristics. As the example of luminescence spectra and luminescence decay caused by the f–f electron transitions shows, optical excitation is the most convenient method for revealing the non-equivalence of activator centers, since the light interacts directly with the activator ions without practically affecting the host matrix [14]. Indeed, it has been observed that different Sm^{3+} centers in ABS glass reveal different luminescence/excitation spectra. For further study, it was natural to choose the glasses activated by Eu and Ce ions as objects of study, since these ions can easily be transferred to their lower valence states [12,15]. Moreover, due to the environment-sensitive $4f-5d$ transition, significantly affected by the nearest environment, the versatile distribution of single Eu^{2+}/Ce^{3+} dopants in multiple cation lattice host can generate multiple fluorescence centers to achieve full visible spectrum emission [16,17].

It is found that the luminescence spectra of glasses doped with Eu^{2+} and Ce^{3+} ions change depending on excitation wavelength (Figure 1). The described dependence means that the radiative energy of electron transitions is correlated with the energy of the levels excited upon absorption of light of a given wavelength. The results confirm the opportunity to observe distinguishable RE local sites in glasses. In addition to the dependence presented, another manifestation of the energy non-equivalence of the activator centers is that with an increase in the wavelength of the detected luminescence, the excitation spectra shift to the longer wavelength side. As it is seen, the maxima of the excitation spectra during registration of Ce^{3+} luminescence in ABS glass at wavelengths of 370 and 500 nm are located at 313 and 340 nm, respectively (Figure 1, *a*). For Eu^{2+} ions, the luminescence band is spread from 400 to 550 nm caused by the excitation with wavelengths from 266 to 400 nm (Figure 1, *b*). The listed features can be explained from a unified point of view, considering them as a consequence of the non-equivalence of the local environment of the activator ions.

At the same time, the non-equivalence of the local environment of Eu^{2+} and Ce^{3+} centers in glass can also

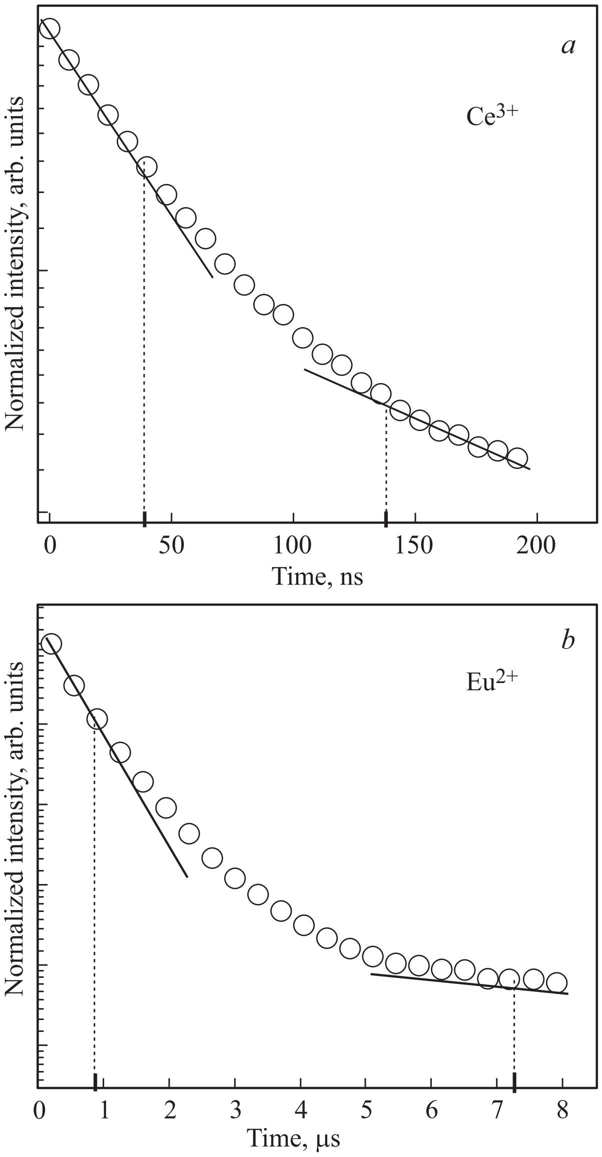

Figure 2. *a*) Luminescence decay curve of Ce^{3+} ions in ABS glass under laser excitation with 266 nm; *b*) luminescence decay curve of Eu^{2+} ions in ABS glass under laser excitation with 355 nm.

affect the decay kinetics of $5d{-}4f$ luminescence. The point is that the probability of such transitions is determined by the degree of contribution of one-electron $4f$ states to the radiative states of the mixed $4f^{n-1}5d$ configuration. In our case, such $4f$ states are the states of free ^{6}P ions for the Eu^{2+} ion and ^{2}D for the Ce^{3+} ion. If the contribution of the ^{6}P and ^{2}D states to the radiative states of the $4f^{n-1}5d$ configuration is different for different centers in the glass (which is logical to assume due to variations in the local environment of the activators), then the probabilities of radiative transitions will also be different. To verify this assumption, we measured the decay curves of Eu^{2+} and Ce^{3+} luminescence in glass. The decay of the luminescence exhibited a clear non-exponential behavior, and the decay rate for Ce^{3+} ions varies on average from ~ 35 ns at the beginning of the decay curve to 140 ns after 220 ns, and for Eu^{2+} ions from 660 ns to almost 8 μs (Figure 2).

It is worth mentioning that the non-exponentiality seen in Figure 2 can only be associated with the kinetic non-equivalence of the activator centers. In this case, it should be remembered that the integrated luminescence intensity at each instant is contributed by the luminescence of centers with a non-equivalent energy structure. In the general case, the radiative probability for different types of activator centers can be correlated with their energy structure, and then the luminescence spectrum will change during the decay process. This means that the decay rate dependence on the luminescence registration wavelength ($\lambda_{\mathrm{em}}^{\mathrm{reg}}$) appears. To prove the existence of non-equivalent distinguishable sites available for Ce^{3+} and Eu^{2+} ions in ABS glass, we measured the evolution of the RE ions lifetime in dependence on $\lambda_{\mathrm{em}}^{\mathrm{reg}}$. Figure 3 exhibits the Ce^{3+} and Eu^{2+} decay curves monitored at different registration wavelengths ($\lambda_{\mathrm{em}}^{\mathrm{reg}}$) with a step of 20 nm. All the decay curves can be well-fitted in a second-order exponential function. It is clearly seen from the Figure 3, *a* and *b* that the lifetime of Ce^{3+} and Eu^{2+} ions at fixed activator concentration shows obvious $\lambda_{\mathrm{em}}^{\mathrm{reg}}$ dependence. Noticeably, it gradually increases from 60 to 120 ns for Ce^{3+}-doped ABS glass as the wavelength continuously varies from 360 to 460 nm. For Eu^{2+}-doped ABS glass, the lifetime increase is observed from 800 ns to 1.3 μs with the wavelength change from 420 to 520 nm. These results are consistent with the fact that the site environment available for Ce^{3+} and Eu^{2+} ions is quite different and the ions can occupy lots of distinguishable local sites in the glass studied.

It can be marked that in the system of non-equivalent centers, there is a correlation between the emission wavelength and the lifetime of ions in the excited state. Such situation arises if the quantum yield of individual types of centers (emitting in different spectral regions) is different, *i.e.*, the total quantum yield depends on the excitation wavelength. The logical consequence of the correlation between energy structures of the emitting centers set with RE ions lifetime is the Eu^{2+} and Ce^{3+} luminescence dependence on the moment of its recording (Figure 4). It is noteworthy that the RE luminescence excited by the Nd : YAG laser pulses shifts with the registration time to longer wavelengths (curve *3* in Figure 4, *a* and *b*) relative to steady-state luminescence (curve *2* in Figure 4, *a* and *b*). At the same time, the measurement at the beginning of the luminescence decay spectrum results in the blue shift in comparison with steady-state luminescence (curve *1* in Figure 4, *a* and *b*).

The long-wavelength shift with time increase could result from the faster decay of its short-wavelength part. As for short-wavelength shift, it should be taken in the mind the law of luminescence flares-up after laser excitation $I(t) = I_{\max}(I - e^{-t/\tau})$, where $I_{\max}$ is the maximum intensity to which the luminescence flares up). In this case, by the end of each exciting pulse, the luminescence intensity

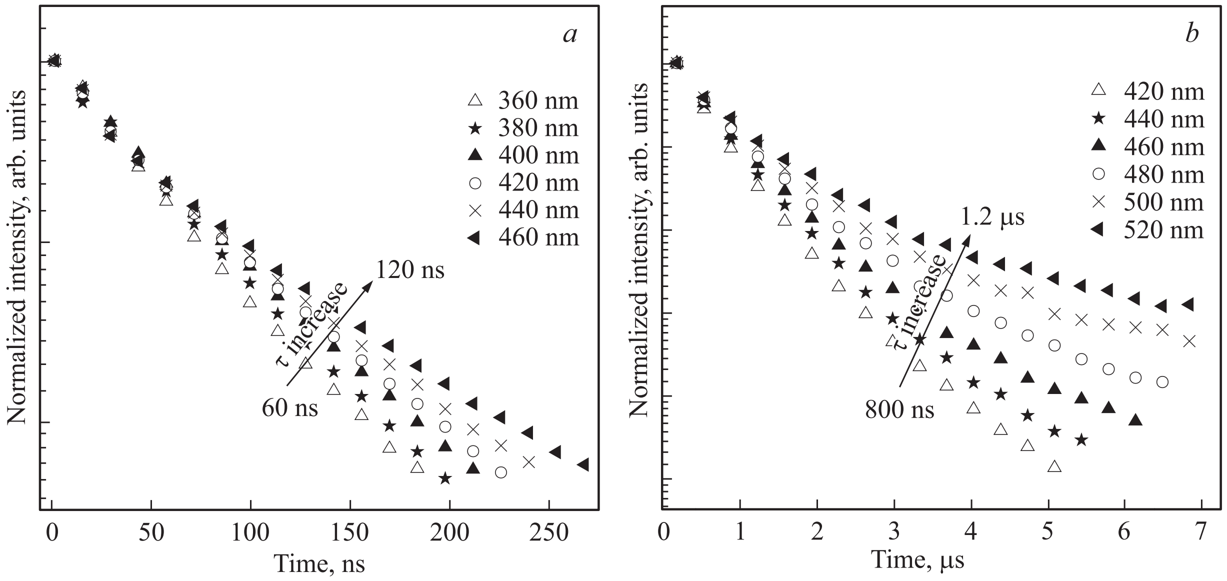

Figure 3. *a*) Luminescence decay curves of Ce^{3+} ions in ABS glass under different registration (λ_{em}^{reg}) wavelengths ($\lambda_{ex} = 266$); *b*) luminescence decay curves of Eu^{2+} ions in ABS glass under different registration (λ_{em}^{reg}) wavelengths ($\lambda_{ex} = 355$).

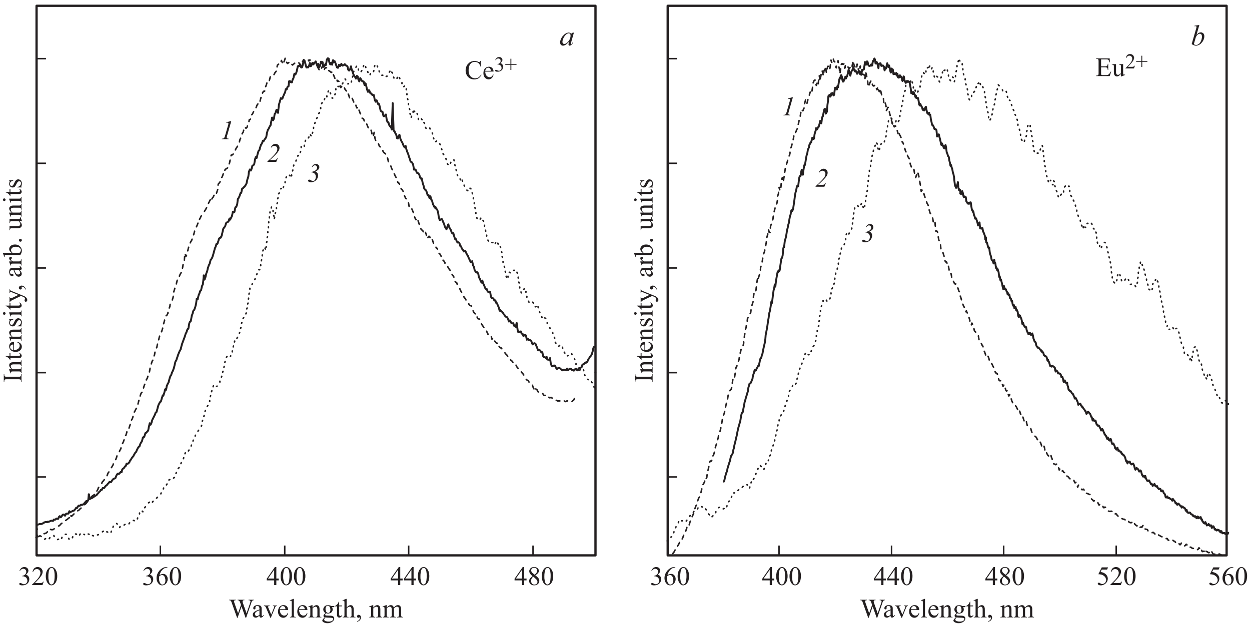

Figure 4. *a*) Ce^{3+} steady-state luminescence spectrum (curve *2*) and luminescence spectra at different stages of the luminescence decay: at the decay beginning (curve *1*) and after 350 ns (curve *3*) ($\lambda_{ex} = 266$ nm) and *b*) Eu^{2+} steady-state luminescence spectrum (curve *2*) and luminescence spectra at different stages of the luminescence decay: at the decay beginning (curve *1*) and after 10 μs (curve *3*) ($\lambda_{ex} = 355$ nm).

of different centers' types is inversely proportional to their lifetime [13]. Thus, the contribution of „short–lived" centers to the total luminescence intensity immediately after the excitation pulse turns out to be noticeably larger than in the case of stationary excitation. The logical consequence of the „short–lived" centers effect is the luminescence UV shift. The results reported manifest that RE local positions in ABS glasses differ from each other in the energy level diagram, as well as in the electron transitions probabilities in the emission. In other words, each type of Eu^{2+} and Ce^{3+} centers in ABS glass is characterized by its own energy level diagrams, its own structure of the luminescence spectra, and as it was described herein above by its own lifetimes.

In summary, all the photoluminescence (PL) data including the decay curves analysis give a strong evidence for the existence of distinguishable local sites available both for Eu^{2+} and Ce^{3+} ions in the glass studied, which is in accordance with the steady-state and time-resolved PL data discussed previously [12,15].

4. Conclusion

The described selection method allows easily to detect and to manage multiply dopant sites with the most appropriative optical characteristics (emission wavelength and emission lifetime) by means of optical excitation. The main findings are listed below:

(1) The excitation and luminescence spectra of Ce^{3+}/Eu^{3+} ions, as well as decay curves, reveal that there are distinguishable local RE cation sites in ABS glasses.

(2) The Ce^{3+} and Eu^{2+} ions show preferable site distribution, which offers the ability to engineer the local site environment available for these ions: the site engineering consequently contributes to emission-on-demand simply by changing excitation wavelength of RE-doped ABS glass and adjusting the experimental conditions for luminescence obtaining.

(3) The results presented provide a very valuable reference for the design of a new generation of luminescent materials.

Conflicts of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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