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OXIDE GLASS WITH MINIMUM DISTANCE 0.67 nm BETWEEN RARE-EARTH ACTIVATORS

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It is shown that glasses in the system $(Ln_xY_{1-x})_2O_3O_3$–Al_2O_3–B_2O_3 are a promising matrix for obtaining highly doped active media with low-efficiency concentration quenching of luminescence. However, because high-frequency vibrational oscillators $[BO_3]$ present in such glasses it is preferable to use activators with an energy gap between a metastable state and a lower state above 8000 cm^{-1} closest to it.

Key words: rare-earth activators, concentration quenching of luminescence, minimum Ln–Ln distance.

Most rare-earth activators in dielectric matrices undergo concentration quenching of luminescence because of cross-relaxation and cooperative non-radiative excitation transfer processes. As a rule, such transfer is due to multipolar interactions of quantum oscillators corresponding to the interacting transitions. The squared matrix element of the Hamiltonian of the multipolar interaction in the adiabatic approximation is characterized by an inverse dependence on the distance between the donor and acceptor of the excitations to the power $m = 6$, 8 and 10, respectively, for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole transitions. For this reason, to minimize the efficiency of the luminescence quenching processes owing to inter-ion excitation transfer the search for matrices giving the maximum value of the indicated distance is topical.

Among such matrices the refractory borates with hantite structure and formula $RM_3(BO_3)_4$, where $R = Y$, Ln and $M = Al$, Cr, Ga, Fe and Sc, draw attention. In this structure the $[LnO_6]$ polyhedra are separated $[BO_3]$ polyhedra, as a result of which the minimum Ln–Ln distance about 5.9 Å [1]. A drawback of these crystals is the relatively efficient multiphoton relaxation between states with energy gap less than $8000 – 10000$ cm^{-1} because of the quite high frequency of the valence vibrations of the B–O bond in $[BO_3]$ polyhedra ($\nu \approx 1300$ cm^{-1}).

The prevailing boron content in the indicated crystals presupposes high glass forming capacity and the possibility of obtaining transparent glasses with the same composition, which is easier to obtain with $M = Al$ (see the hantite formula presented earlier). A potential advantage of such glasses is a decrease of the concentration of vibrational oscillators $[BO_3]$ as a result of some of the boron transitioning from triply into quadruply coordinated, for which the frequency of the valence vibrations of the B–O bond is about 1100 cm^{-1}.

Using luminescence methods to analyze the distribution of the active impurity in solids [2], we have shown that with a transformation of the hantite-like polycrystals $Sm_xY_{1-x}Al_3(BO_3)_4$ into glass with the composition (mol.%) 12.5 $(Sm_xY_{1-x})_2O_3$, 37.5 Al_2O_3 and 50 B_2O_3, which occurs at temperature about 1470°C, the structure of the distribution of the rare-earth elements in the matrix is preserved while the minimum distance between the ions Sm–Sm increases to 6.7 Å, which is a record for oxide matrices [3]. This result shows that in hantite-like glasses there are practically no Ln–O–Ln bonds, i.e., despite the disordered structure of the matrix the $[LnO_n]$ polyhedra are isolated from one another (they have no vertices in common). As expected, some $[BO_3]$ polyhedra transform into $[BO_4]$ and the quantum yield of luminescence increases correspondingly [3, 4].

Subsequent studies showed that an increase of the B_2O_3 concentration significantly lowers the synthesis temperature and reduces the proneness of the glass toward crystallizing on heating, but has a weak affect on the Ln–Ln distance. Since it is possible to introduce into such glass high lanthanide concentrations ($N_{Ln} \approx 4.5 \times 10^{21}$ ions/cm^3) it can be recommended as matrix for obtaining highly doped optical

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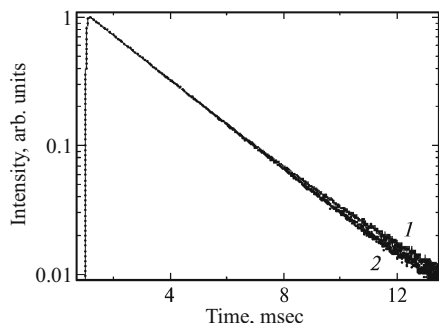[4] E-mail: golubev_muctr@gmail.ru.

Fig. 1. Kinetics of luminescence decay of Tb-containing hantite-like glass with detection at wavelength 545 nm. Terbium ion concentration: *1*) 1×10^{20} cm^{-3}, *2*) 30×10^{20} cm^{-3}; excitation pulse duration at half-height — 1 μsec.

materials, including active laser materials with low concentration quenching of luminescence. However, since the fraction of high-frequency vibrational oscillators $[BO_3]$ in such glass is significant, it is preferable to use activators with energy gap $\Delta E > 8000$ cm^{-1} between the metastable state and the state closest to it.

One of the activators satisfying this condition is the ion Tb^{3+}, for which ΔE in the fundamental luminescence transition $^5D_4 \rightarrow {}^7F_j$ is about 14,700 cm^{-1}. However, these ions are subject to quite efficient concentration quenching of luminescence, for which the most likely scheme for most matrices is Tb^{3+} ($^5D_4 \rightarrow {}^7F_3$) : 3Tb^{3+} ($^7F_6 \rightarrow {}^7F_1$). As a result of such quenching the average duration of the luminescence quenching of Tb^{3+} ions, for example, in a glass matrix (mol.%) 58 SiO$_2$, 23 CaO, 5 Al$_2$O$_3$, 4 MgO and 10 NaF with Nb increasing from 0.9×10^{20} to 31×10^{20} ions/cm^3 decreases approximately 1.5-fold [5]. However, in hantite-like glass, for a similar change in N_{Tb}, as follows from Fig. 1, there is no acceleration of the quenching process — the decay law remains exponential while the decrease of the decay constant does not exceed 1% (from 2.56 to 2.54 msec).

Another positive quality of this matrix is the quite short-wavelength position of the fundamental absorption edge — the linear absorption index $k = 20$ cm^{-1} is reached at $\lambda = 235$ nm, which makes it possible to excite rare-earth activators into excited interconfiguration transition charge transfer bands.

It can be asserted on this basis that glass in the system $(Ln_xY_{1-x})_2O_3$–Al$_2$O$_3$–B$_2$O$_3$ is a promising matrix for obtaining highly doped active media with low-efficiency concentration quenching of luminescence.

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