Rayleigh scattering intensity and radiationless losses from the metastable state of Nd^{3+} in laser silicate glasses

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(Submitted March 12, 1975)
Zh. Eksp. Teor. Fiz. **69**, 540–546 (August 1975)

Studies of the luminescence spectra of complex neodymium-activated laser glasses have established that the silicate glasses LGS-28 and ED-2 have different luminescence parameters. The fine structure of Rayleigh scattering by these multicomponent systems has been investigated. For the purposes of comparison, the Rayleigh scattering spectra of single-component glass, i.e., fused quartz, have also been obtained. The relationship between the quantum yield of luminescence from the metastable state of Nd^{3+} and the intensity of the central component of the Rayleigh spectrum has been found. It is shown that scattering by microinhomogeneities in the multicomponent systems, which are connected with the presence of several components, may be quite weak and in such systems the quantum yield approaches unity. It is established that multicomponent systems in which scattering by such microinhomogeneities is substantial have a low quantum yield. Owing to the microinhomogeneous structure of these systems, the activator ions are distributed nonuniformly in the matrix, forming regions of enhanced concentration in which the number of multipole interactions between active particles is substantial, even for low activator concentrations, and this leads to the degradation of electron excitation into thermal vibrations.

PACS numbers: 42.60.Gd, 78.60.Dg, 42.70.Ce

The mechanisms leading to radiationless losses from the metastable state of Nd^{3+} in laser glasses have not as yet been established.[1] It was suggested in[2] that the low luminescence quantum yield of silicate glasses is connected with the interaction between active ions, the effectiveness of which is quite high even at very low concentrations because of the nonuniform distribution of Nd^{3+} in the matrix. This conclusion was based on studies of the kinetics of decay of the excited metastable state of Nd^{3+} in LGS-28 silicate glasses.

It was found that the contribution of radiationless decay to deactivation of the excited state had the form

$$I(t)=I_0e^{-\Pi(t)},\quad \Pi(t)=\gamma\sqrt{t}+\bar{w}t. \tag{1}$$

where γ characterizes direct donor-acceptor interactions. In the case of Nd^{3+}, this is the cross-correlation through the intermediate $^4I_{15/2}$ level; $\bar{w}$ is the probability of migration to the acceptor and radiationless loss on it. The ion Nd^{3+} can act both as a transporter and an acceptor of energy.[3] The connection between γ and $\bar{w}$, on the one hand, and the interaction parameters, the cross-correlation probabilities w_{cr}, and the energy-migration probabilities w_m, on the other hand, is as follows:[2-4]

$$\gamma=\frac{4}{3}\pi^{3/2}(c_{DA})^{1/2}n_A,\quad \bar{w}=\pi\left(\frac{2\pi}{3}\right)^{5/2}(c_{DA})^{1/2}(c_{DD})^{1/2}n_An_D. \tag{2}$$

In the case of the dipole-dipole interactions which take place in Nd^{3+},[3]

$$w_{cr}=c_{DA}/R_{DA}^6,\quad w_m=c_{DD}/R_{DD}^6, \tag{3}$$

where c_{DA} and c_{DD} are the parameters of the donor-acceptor and donor-donor interactions, respectively; R_{DA} and R_{DD} are the donor-acceptor and donor-donor distances, respectively, and n_A and n_D are the acceptor and donor densities.

If cross-correlation through the intermediate level of Nd^{3+} is responsible for the degradation of electron excitation into thermal vibrations, then $n_A = n_D = n_0$ and $R_{DA} = R_{DD}$,[3] where n_0 is the total activator concentration. A concentration dependence of the form given by (2) has been observed for LGS-28 glass in the concentration range 5–16 wt.% Nd^{3+}.[2] For concentrations of 0.05–2%, the form of the function $\Pi(t)$ is the same, but γ and $\bar{w}$ are no longer functions of concentration. This unexpected result has led to the suggestion that the activator is nonuniformly distributed in the matrix, even when it is present in small amounts, and forms regions of enhanced concentration (clusters). An increase in the concentration from 0.05 to 2% then leads to only an increase in the number of such regions whereas the mean distance between the interacting ions in the regions remains the same. The small separation between active ions in the clusters as compared with the statistical average of this distance evaluated over the entire medium gives rise to a substantial increase in the effectiveness of multipole interactions and thus to a degradation of electron excitation into thermal vibration, a reduction in the quantum yield, and a nonexponential decay of excited states.[2,3] An exponential decay of excited states with the radiation constant, and a quantum yield of more than one, must then indicate that the activator is statistically distributed, i.e., there are no clusters. If this description does, in fact, correspond to reality, then glasses with a low quantum yield should exhibit a relatively higher intensity of Rayleigh scattering because the clusters must, in one way or another, be connected with the presence of microinhomogeneities in the glass.

In the present paper, we report the results of experiments which have established the connection between the Rayleigh intensity I_R and the quantum yield η of luminescence from the metastable state of Nd^{3+} in silicate glasses.

We have determined the quantity

$$\eta=S_1/S_2, \tag{4}$$

for a series of glasses with different compositions. In this expression, S_1 is the area under the curve showing the decay of the excited state for the specimen under investigation, and

$$S_2=I_2\int_0^\infty e^{-t/\tau_0}dt.$$

The normalization condition is $I_2 = I_1$, where I_1 is the luminescence intensity at $t = 0$. The values of $\tau_0 = (\Sigma A)^{-1}$

for the specimens which we have investigated are given in[5,6], where ΣA is the total probability of radiative transitions from the metastable state to all the lower levels of the ground state multiplet, so that τ_0 is the radiative lifetime of this metastable state. The kinetics of the decay of the excited state was examined by the method described in[2]. The uncertainty in η did not exceed 10%. It turned out that the values of η for all the silicate glasses which we have investigated lay between 0.4 and 0.6. For the LGS-28 glass (the kinetic measurements reported in[2] were made on this glass), it was found that η was 0.45 for Nd^{3+} concentration of 2% by weight, and remained practically constant as the concentration was reduced. The exception to this type of behavior is the ED-2 silicate glass with activator concentration of 1% by weight, for which $\eta \approx 1$.

FINE STRUCTURE OF RAYLEIGH SPECTRA AND DISCUSSION OF RESULTS

The fine structure of the Rayleigh scattering spectra was examined with the spectrometer described in detail in[7]. This system incorporates photon counting, a piezoelectrically scanned Fabry-Perot interferometer, and a digital multichannel analyzer. The source of exciting radiation was the single-mode He-Ne laser working at $\lambda = 6328$ Å. The scattering angle was 90°. The polarization of the exciting radiation was perpendicular to the plane of scattering. The detector of the spectrometer recorded both polarization components. The absolute intensities of the central (unshifted) components of the scattered spectra were determined by the method described in[8-10]. It involves the determination of the ratio R of the intensities of the central component (I_R) of the scattered spectrum to the Mandel'shtam-Brillouin intensity (I_{MB}). If we know the refractive index n, the specimen density ρ, the optoelastic constants P_{12}, and the velocity V_L of propagation of longitudinal ultrasonic waves, we can calculate the Mandel'shtam-Brillouin scattered intensity which is proportional to the extinction coefficient α_{MB}:

$$\alpha_{MB} = \frac{8\pi^3}{3} \frac{kT}{\lambda^4} \frac{n^8 (P_{12})^2}{\rho V_L^2}. \tag{5}$$

By measuring $R = I_R/I_{MB} = \alpha_R/\alpha_{MB}$, and calculating α_{MB} from (5), we obtain the extinction coefficient α_R for the central component.1) In this type of experiment, one need not bother to stabilize the intensity of the exciting radiation.

In the laser glasses which we have investigated, $R \sim 100$. Under these conditions, the intensity of the central component was not high enough to produce counting losses, and 200—250 storage cycles did not overload the analyzer store so that the signal-to-noise ratio that could be achieved in measurements of the Mandel'shtam-Brillouin component intensities was at least 15. We used SZS-14 filters to reduce the luminescence intensity, which meant that the signal-to-noise ratio was somewhat lower than in[10]. We examined different specimens of LGS-28 glass with activator concentrations of 0.05, 0.1, 0.3, 1, 2, and 5% Nd_2O_3 by weight, specimens of the ED-2 glass with Nd^{3+} concentration of 1% by weight, and fused quartz. The specimens were 1 × 1 × 1 cm cubes with plane-parallel faces. The scattered radiation was examined repeatedly at different points in the specimen. The spread in the values of R did not exceed 10%. It turned out that, in the case of LGS-28 glass, the value of R was independent of the activator concentration and amounted to 135 ± 10. This showed that the activator did not affect the character of the microinhomogeneities present in the glass in this concentration range.

The values of R, α_{MB}, and α_R for LGS-28, ED-2, and fused quartz are listed in the table. The parameter α_{MB} was calculated from (5). The necessary constants for fused quartz can be found in[11] and for LGS-28 in[12,13]. The parameters of a glass characterized as "type E" are given in[14] together with the composition of this glass. It is clear that it is identical in composition with the ED-2 glass.[15] The data on α_R given in the table were also checked against directly measured intensities of the central components of the scattered spectra for all the specimens under investigation. The results agreed to within about 10%. The data listed in the table indicate that ED-2 is a highly homogeneous glass.

The intensity of the central component in the scattered spectrum of amorphous bodies can, in fact, be due to a number of factors, including "frozen-in" fluctuations of density, orientation, structural entropy, deformation, and stress. In multicomponent systems, there is also scattering by "frozen-in" concentration fluctuations. In silicon glasses, and in fused quartz, the intensity of the central component of the fine structure, I_R, is substantially greater than the theoretical prediction.[16] The reason for this discrepancy is the presence of microinhomogeneities of ~100 Å in the glass. These have been detected, for example, by small-angle x-ray scattering and by electron microscopy.[17]

Attempts have been undertaken to explain these microhomogeneities by "frozen-in" fluctuations.[18] It is shown in[16,19,20] that, because of the rapid spreading of fluctuations in pressure and entropy, the density fluctuations cannot be "frozen-in." According to Fabelinskiĭ,[16] the question as to whether concentration fluctuations can be "frozen-in" in silicate glasses is equivalent to the question as to what is the relevant value of the diffusion coefficient for a particular component of the silicate glass. Until quite recently, there have been no data on the diffusion coefficient D in glasses, and the author of[16] estimated the dissipation time δ for concentration fluctuations by assuming that $D \sim 10^{-8}$ cm²/sec. This is characteristic for the diffusion of salt into salt, and the result of the calculation was $\delta \sim 10^{-4}$ sec. Hence it was concluded that the freezing-in of concentration fluctuations was impossible. However, the diffusion coefficient D has now been measured for silicate glasses and has been found to be much lower. Thus, Andreev et al.[21] have found that the values of D for silicate glasses vary from 5×10^{-18} to 9×10^{-15} cm²/sec as the temperature is increased from 550 to 560°C, and the corresponding values of δ are 300—0.2 h.

Consequently, the observed microinhomogeneities can, in fact, occur as a result of the "freezing-in" of concentration fluctuations. It is clear that the frozen-in concentration fluctuations can occur only in the multicomponent system and are therefore absent from fused

Material	η	$R = I_R/I_{MB}$	α_{MB}, cm⁻¹	α_R, cm⁻¹
Fused quartz	—	55	$0.40 \cdot 10^{-6}$	$2.2 \cdot 10^{-5}$
LGS-28 glass, 0.05–2% by weight Nd^{3+}	0.45	135±10	$0.396 \cdot 10^{-6}$	$5.35 \cdot 10^{-5}$
ED-2 glass 1% by weight Nd^{3+}	1	120±10	$0.243 \cdot 10^{-6}$	$2.92 \cdot 10^{-5}$

quartz. Experimental results confirm that the intensity of the central component of the Rayleigh spectrum in the case of multicomponent systems is much greater than for the single-component systems. Thus, it is shown in[10] that the value of α_R for fused quartz is lower than the value for multicomponent glasses by a factor of at least two. On the other hand, the contribution of all the other scattering mechanisms, i.e., other than the "frozen-in" concentration fluctuations, in single- and multicomponent silicate systems can be regarded as approximately the same. We are thus naturally led to the conclusion that the difference between the intensity of the central components of the Rayleigh spectrum of multicomponent glasses and fused quartz is largely due to the "frozen-in" concentration fluctuations.

It is clear that the ratio of the values of α_R for ED-2 and for fused quartz is 1.3, whereas for LGS-28 and many other glasses of complex composition, this ratio is 2.5 or more.[10] This leads us to the conclusion that ED-2 is a highly homogeneous glass.

The ED-2 glass has scattering parameters very different from other glasses of complex composition. It would appear that it has unusually small fluctuations of refractive index connected with the frozen-in concentration fluctuations and characteristic of multi-component systems. On the other hand, in LGS-28 glass and in other multicomponent systems, the "frozen-in" concentration fluctuations provide the dominant contribution to Rayleigh scattering.

This unique property of ED-2 is not the only remarkable property of this glass. As noted above, it is the only silicate glass that we are aware of, for which the quantum yield is close to unity. Thus, measurements of η performed in the present work on seven specimens of silicate-based laser glasses showed that they lay between 0.4 and 0.6. Other workers have also shown that the quantum yield of luminescence from the metastable state of Nd^{3+} in silicate glasses is substantially less than unity.[22,23]

The combination of these two properties in ED-2 glass does not seem to be accidental. When an activator is introduced into an inhomogeneous system, the activator ions are distributed among the different phases of the microheterogeneous structure in accordance with the well-known laws of chemical thermodynamics. The activator can enter the phases present in "pure" glass, but it is also possible that the activator may form a new phase by combining with certain components of the glass. If the coefficients representing the distribution of the activator among the phases of the system are very different from unity, one of the phases will be enriched and another depleted in ions of the impurity introduced into the system.[24] In the phase which concentrates the activator, the mean distance between the impurity ions will be much smaller than the average distance evaluated over the entire system. This is, in fact, the assumption made in the model of radiationless losses from the metastable Nd^{3+} state in the laser silicate glass proposed in[2] and mentioned above.

It was demonstrated experimentally in[25] that in glasses subjected to microstratification, the Nd^{3+} ions preferentially entered the microphase enriched with the alkali, i.e., the situation described above is, in fact, realized. The separation between activator ions in liquating glass was reported in[26] as being small in comparison with the statistical average. Therefore, the Nd^{3+} ions enter certain definite places in the microheterogeneous structure of a complex glass in a preferential fashion, and if the system contains strong "frozen-in" concentration fluctuations, the Nd^{3+} ions will also exhibit these fluctuations, i.e., there will be clusters in which luminescence will be subject to concentration quenching and the quantum yield will be low. This situation occurs, for example, in the LGS-28 glass. On the other hand, when the frozen-in concentration fluctuations in a multicomponent system are small, the corresponding fluctuations in Nd^{3+} concentrations are also small, and the quantum yield turns out to be high.

It is important to note that the nature of the frozen-in concentration fluctuations in glasses, which leads to the appearance of inhomogeneities of ~100 Å, may be different, depending on the composition of the glass and the technology used to manufacture it. It may involve both initial liquation and initial crystallization stages. The fact that γ, $\overline{w}$, and α_R are independent of activator concentration in LGS-28 suggests that the Nd^{3+} ions enter preferentially one of the microphases of this multicomponent glass.

Our investigations thus lead us to the conclusion that there is a connection between the quantum yield of luminescence from the metastable state of Nd^{3+} in silicate multicomponent glasses and the intensity of the central component in the Rayleigh spectrum. The multicomponent system which contains substantial frozen-in concentration fluctuations has a low quantum yield. Because of the microinhomogeneous structure, the activator ions in this system are also nonuniformly distributed, and this is in agreement with the mechanism of radiationless excitation losses from the metastable state, proposed in[2]. It is now established that the frozen-in concentration fluctuations in multicomponent systems can be small and that, in such systems, the quantum yield turns out to be close to unity.

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1) Since $R \gg 1$ in glasses, the coefficient α_R is practically equal to the total extinction coefficient.

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Translated by S. Chomet
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