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The Influence of the Composition of Glasses Activated with Neodymium on Their Absorption Spectra and Luminescence Duration

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In connection with the development of quantum optical generators, interest in glasses containing rare-earth elements has increased considerably. The use of glass as a medium for introducing active additives is due to the good solubility in it of oxides of rare-earth elements and, consequently, to the possibility of obtaining materials with a high degree of optical homogeneity. Of considerable importance here is also the possibility of producing articles of any geometrical shape and size. Radiation of high power (of the order of several hundred joules) has been obtained in silicate glass ([1]), and in a number of cases the generation threshold in glasses is lower than in ruby crystals.

Among the ions of rare-earth elements, the trivalent neodymium ion possesses the most favorable properties for obtaining stimulated emission, since population inversion of the energy levels is achieved comparatively easily for it and cooling to low temperatures is not required. In this connection, much attention is being devoted to the investigation of the spectroscopic properties of glasses activated with neodymium.

The principal absorption bands of trivalent neodymium lie in the visible and near-infrared regions of the spectrum, whereas luminescence is observed in the IR region at wavelengths of 0.9; 1.06; 1.3; and 1.9 μ, the band at 1.06 μ having the greatest intensity. The first report of obtaining stimulated emission in glass activated with neodymium was made in ([2]). The initial glass, of the barium crown type, had the composition: 59.0 SiO_2; 25.0 BaO; 15.0 K_2O; and 1.0 Sb_2O_3 (wt.%). Stimulated emission was obtained at a wavelength of 1.06 μ. The duration of the emission proved to be 560 μsec, which is in good agreement with the value of 600 μsec calculated by the author on the basis of the absorption and luminescence spectra.

In a glass of composition (mol.%) 56.7 SiO_2; 5.7 Al_2O_3; 29.6 MgO; 7.4 Li_2O, stimulated emission from two rare-earth ions—neodymium and ytterbium—was obtained at the temperature of liquid nitrogen ([3]). The bleaching duration of the samples during generation was 1200 μsec, whereas the luminescence duration

of glass activated only with neodymium was 350 μsec.

In ([4]) the possibility of obtaining stimulated emission in neodymium-containing glass at a wavelength of 0.9180 μ is reported. The glass used had the composition (wt.%): 71 SiO_2; 1.0 Al_2O_3; 12.0 CaO; 15.0 Na_2O; and 1.0 Sb_2O_3. The experiments were carried out at the temperature of liquid nitrogen.

Investigation of glasses of various compositions (phosphate, silicate, and borate) with different concentrations of neodymium (from 0.1 to 10.0 wt.%) showed that barium crowns of complex composition with a neodymium concentration of about 4.0 wt.% have the best characteristics ([5]). Glass,

used for observing stimulated emission had a luminescence duration on the order of 700 μsec.

A spectroscopic study of simple-composition glasses ([6]) activated with neodymium made it possible to construct a scheme of the lower energy levels of neodymium and to establish a number of regularities in the changes of the absorption and luminescence spectra of glasses as a function of the composition and structure of the glass, as well as of the neodymium concentration and the temperature of the surrounding medium. It was established that the structure of the spectra and the lifetime of the excited state depend to a significantly greater degree on the type of glass-forming element than on the type of modifier ions. The lifetime of the excited state, as a function of the glass composition, is in accordance with the change in the width of individual absorption bands.

Table 1

Composition designation	Mol. %, R_2O	Mol. %, SiO_2	Wt. %, Na_2O	Wt. %, SiO_2	Wt. %, K_2O	Wt. %, SiO_2	Wt. %, K_2O	Wt. %, GeO_2
1–1	50,0	50,0	50,8	49,2	61,0	39,0	47,4	52,6
1–2	33,3	66,7	34,0	66,0	43,8	56,2	31,1	68,9
1–3	25,0	75,0	25,5	74,5	34,3	65,7	23,4	76,6
1–4	20,0	80,0	20,5	79,5	28,1	71,9	18,4	81,6
1–5	15,3	84,7	17,1	82,9	23,8	76,2	15,3	84,7
1–6	14,3	85,7	–	–	20,8	79,2	13,0	87,0
1–7	12,5	87,5	12,7	87,3	18,3	81,7	11,4	88,6
1–8	11,1	88,9	–	–	16,4	83,6	10,1	89,9
1–9	10,0	90,0	10,3	89,7	14,8	85,2	9,0	91,0
1–11	8,3	91,7	–	–	12,5	87,5	7,5	92,5

The width of the absorption bands is determined by the type of modifier ions introduced and by the structure of their electron shells. It was established that,

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

all other conditions being equal, the broader the absorption band, the shorter the luminescence duration.

The aim of the present investigation was to study the absorption spectra and luminescence duration of silicate and germanate glasses activated with neodymium as a function of the ratio, in the glass composition, of the oxides of glass-forming agents and modifiers, as well as of the neodymium concentration. Simple two-component glass compositions were selected for the investigation. The glasses were melted in corundum crucibles in a laboratory silite furnace in quantities of 20 g at temperatures of about 1300–1500°. Chemically pure materials were used to prepare the batch. Neodymium oxide was introduced into the glass in an amount of 2 wt.% in excess of 100%. The neodymium oxide content in the reagent was 99.98%. The iron content in the glass was reduced to a minimum.

The absorption spectra of the glasses were obtained on SF-10 and SFD-2 spectrophotometers. To eliminate the influence of sample thickness and density, the measured optical-density values were reduced to unit thickness and density of the glass ($E = D/l \cdot d$). The luminescence of the samples was excited by an IFK-2000 lamp. The exciting radiation passed through SZS-8 and SZS-18 filters. IKS-1 and KS-19 filters were placed in front of the radiation receiver (FEU-28).

Table 1 gives the compositions of glasses obtained in the systems Na_2O–SiO_2; K_2O–SiO_2 and K_2O–GeO_2, as well as their conventional designations, representing the number of moles of glass-forming oxide per one mole of modifier. For the indicated glass compositions, absorption spectra were obtained, the values of specific absorption at the maxima of the main absorption bands were measured, and the luminescence-duration values at room temperature were determined. Since glasses with a high alkali content (compositions 1–1, 1–2) are chemically unstable, their absorption spectra were not investigated.

The finest structure of the absorption spectra was observed for potassium silicate glasses. With increasing alkali content in silicate systems, the absorption bands broaden and the magnitude of absorption at the band maximum changes. The largest values of E are observed for glasses containing more than 20 mol.% alkali, and the lowest values of E are found in silicate systems for compositions with a high SiO_2 content.

The absorption bands in germanate glasses are broader and are shifted toward longer wavelengths by 1-2 mμ. In comparison with the corresponding compositions in the potassium silicate system, germanate glasses differ in the structure of their absorption spectra. At a high content of germanium dioxide in the glass composition (compositions 1-9,

Fig. 1. Change in the luminescence lifetime of glasses as a function of compo-

sition. The neodymium content is 2 wt.%.
1 –glasses in the K_2O—SiO_2 system; 2 –glasses in the Na_2O—SiO_2 system; 3 –glasses in the K_2O—GeO_2 system.

Fig. 2. Change in the luminescence lifetime as a function of neodymium oxide content.
1 –glass of composition $1K_2O \cdot 7SiO_2$; 2 –glass of composition $1K_2O \cdot 3GeO_2$.

1-11) a strongly blurred structure of the absorption bands is observed. With increasing potassium oxide content, the absorption bands are gradually resolved. The fine structure of the spectra in the germanate system is observed for glass of composition 1-3. The change in the absorption spectra also consists in a redistribution of the intensity of the absorption bands. A sharp change in absorption intensity occurs at the wavelength 573 mμ; in glass of composition 1-11 the band at 573 mμ is not resolved and has the lowest value of E. With increasing potassium oxide content, absorption at the maximum of the band at 573 mμ increases and reaches its maximum value for composition 1-3. At the same time, the magnitude of absorption at 586 mμ changes only slightly.

Figure 1 shows the change in the luminescence lifetime (τ) of the glasses as a function of composition. This dependence is most clearly expressed for the potassium silicate system. The maximum value of the luminescence lifetime (about 800 μsec) was obtained for composition 1-7 (12.5 mol.% K_2O and 87.5 mol.% SiO_2). For the sodium silicate system, the values of τ at the same molecular ratio of oxides are lower, and the course of the curve is smoother. For the potassium germanate system, as the composition changes, the luminescence lifetime values also pass through a maximum; however, this maximum is shifted toward compositions with a higher alkali content. The maximum value of τ in the germanate system, equal to 580 μsec, was obtained for composition 1-3 (25 mol.% K_2O and 75 mol.% GeO_2).

In the potassium silicate system, a study was also carried out

of the luminescence lifetimes of the indicated compositions at contents of 1 and 4 wt.% Nd_2O_3. As the results of the study showed, the dependences of the luminescence lifetime on composition in these cases have the same character as at a content of 2 wt.%, and the maximum value of τ is observed for glass of the same composition, 1-7. However, the luminescence lifetime of glasses of composition 1-7 changes with changing Nd_2O_3 content owing to concentration quenching. For compositions $1K_2O \cdot 7SiO_2$ and $1K_2O \cdot 3GeO_2$, the luminescence lifetime was studied as a function of neodymium content. The neodymium concentration was varied from 1.0 to 10 wt.%. The resulting dependences of the luminescence lifetime on neodymium content are shown in Fig. 2. As was to be expected, with increasing neodymium content in the glass composition, τ decreases owing to concentration quenching. In germanate glass, the decrease in luminescence lifetime occurs more sharply with changing neodymium oxide content than in silicate glass.

Discussion of the results obtained may be undertaken on the basis of ideas about

the coordination arrangement of ions in the glass structure and the interaction of neodymium ions with the surrounding oxygen ions. A change in the structure of the absorption spectra reflects a change in the interaction of neodymium ions with oxygen ions. Strong Nd–O interaction leads to fine resolution of the absorption spectra, whereas a decrease in Nd–O interaction leads to broadening of the absorption bands. This dependence can be observed in going from potassium silicate glasses to sodium glasses. Owing to the stronger field of the sodium cation, the Nd–O interaction in sodium silicate glasses is weaker than in potassium silicate glasses, as a result of which the absorption bands are broader and, in a number of cases, are not even resolved. Correspondingly, the luminescence lifetime in sodium glasses is lower than in potassium glasses. At the same time, as our investigations showed, the luminescence lifetime of rubidium glasses is considerably higher than that of potassium glasses. The broadening of the absorption bands with an increase in the alkali content in the glass composition may be caused by an increase in the number of neodymium ions located in nonequivalent regions of the glass structure.

In glasses of the germanate system, diffuse absorption spectra are observed for glasses with a high content of germanium dioxide. With an increase in the content of potassium oxide in the glass, the Nd–O interaction increases, which leads to a finer structure of the absorption spectra and to an increase in the luminescence lifetime.

It may be assumed that a change in the composition of the glass leads to a rearrangement of the coordination polyhedra around the neodymium ions, to a change in the interaction of neodymium ions with oxygen ions and, ultimately, to a change in the absorption spectra and luminescence lifetime.

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Note: Figure translations are in progress. See original paper for figures.