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Photoluminescence of Gallate Glass-Ceramics: Al2O3 Influence

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Abstract The influence of Al2O3 as an additive and the heat-treatment regime on the luminescence spectra of gallate glass-ceramics was investigated. It is shown that its luminescence efficiency can be enhanced by changing the submicron-inhomogeneous structure of the initial glasses.

Text

The precipitation of nanocrystals (NC) of wide-gap semiconductors in the interior volume of glass affords great applied prospects owing to their unique optical properties and the heightened chemical and thermostability of the glassy matrix as well as its high transparency and manufacturability. Of special interest are glasses with the NC phases β-Ga2O3 and γ-Ga2O3, characterized by a wide bandgap Eg ~ 4.5 – 4.9 eV and luminescence in long wavelength UV and visible ranges. The high-value of Eg makes it possible to record the UV radiation of the solar-blind range, which can be used for monitoring the technical state of high-voltage equipment, assessment of the state of the ozone layer, fire-prevention monitoring, and so on [1].

The probability of radiative recombination in semiconductors is well-known to be a function of the donor–acceptor distance, i.e. it depends on the size of the NC [2]. According to our data [3] the formation of NC γ-Ga2O3 in low-alkali gallium germanium silicate glasses is preceded by phase separation of the liquid type, which results in the formation of Ga2O3-enriched regions of inhomogeneity with diameter about 8 nm. As a result the average diameter of NC γ-Ga2O3 in a transparent glass-ceramic obtained using a one-step regime is at least about 6 nm. In addition an appreciable fraction of larger-size NC, in which the probability of radiative recombination is considerably reduced, is formed [4]. Although the use of a two-step heat treatment decreases the

relative content of such NC, raising the efficiency of luminescence, its subsequence increase is possible only after suppression (at least partial) of the liquid immiscibility in the original gallium-germanium silicate glasses. The introduction of Al2O3 into their composition is expected to weaken the liquation processes [5, 6] and therefore diminish the regions of inhomogeneity formed on cooling of the melt. This will make it possible to reduce the size of the precipitated NC γ-Ga2O3 and increase the integral intensity of the luminescence band. The present work is devoted to checking this supposition of ours using the method of 'additions' and 'substitutions' when introducing Al2O3.

Glass with Al2O3 was synthesized in a about 40 ml platinum crucible, placed in a furnace with SiC heaters, at 1480°C (60 min). At the completion of the melting the melt was poured out of the crucible onto a metal plate and pressed by another plate to thickness about 2.5 mm. The reagents were ultrapure grade SiO2 and GeO2 and chemically pure grade Ga2O3, Li2CO3, and Na2CO3. Al2O3 was added in the amount 2.5% (molar content) via Al(OH)3 (analytically pure grade) either above 100% or replacing some of the Ga2O3 in the composition of the glass. The obtained glasses are designated below as 20Ga–2.5Al and 17.5Ga–2.5Al, respectively. For comparison, a homogeneous glass with no Al2O3 (20Ga–0Al in what follows) was used, melted in an amount sufficient to determine heat-treatment regimes and evaluate reproducibility in determining the desired characteristics. The synthesis and properties of this glass are described in [7] in comparison with the glass synthesized by the melt quenching method.

Differential scanning calorimetry (DSC) was performed using an STA-449 F3 Jupiter (Netzsch) thermal analyzer for a about 25 mg glass monolith with heating rate 10 K/min in Ar current and platinum crucibles with lids. Heat treatment of glasses with one mass (about 1.5 g) was conducted in a Vario 200 (Zubler) furnace for 15 min, with the exception of prolonged low-temperature treatment (615°C, 3.5 h) in a muffle furnace (Termokeramika). The samples were placed in the furnace at the treatment temperature, and at the completion of the heating schedule they were immediately removed from the furnace, and then ground and polished in the same regime.

X-ray phase analysis (XPA) of the powders of heattreated glasses was performed with a D2 Phaser (Bruker) x-ray diffractometer (CuKα radiation) in the range of angles 10 – 100° with step 0.02° and dwell time 1.5 sec at a point. During the photographing the sample rotated at speed 30 rpm. The region of coherent scattering was calculated from the width of the diffraction reflection at about 64° (2θ), using Scherer's equation [8]. The degree of crystallinity of the glasses was calculated from the relation

100×(Ap/Ax),

where Ap is the integral area of the diffraction reflections and Ax is the integral area of the entire x-ray diffraction pattern (minus the background).

The light attenuation spectra of the heat treated glasses were recorded with a UV-3600 (Shimadzu) spectrophotometer. The luminescence spectra with stationary excitation in the UV range by radiation from a xenon lamp were obtained using a spectral/analytic system based on a

MS3504i (SOL instruments) monochromator/spectrograph. The change in the integral intensity of the luminescence for one and the same section of the GCM during its positioning and taking into account the drift of the system was less than 5% over the time required to photograph the entire series of samples.

The introduction of Al_2O_3 into the glass composition increases the low-temperature viscosity, displacing the glasstransition temperature (the starting point) and in one case also the maximum of the exothermic peak to higher temperatures (Fig. 1). In addition the significant narrowing of the exo-effect and growth of its intensity indicates an increase in the rate of crystallization of the glass into whose composition Al_2O_3 was introduced in an amount above 100%.
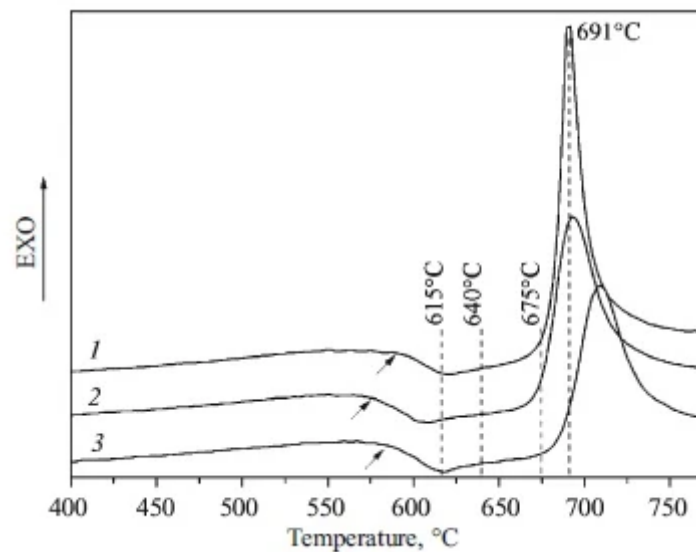

Figure 1. DSC curves of the glasses 20Ga–2.5Al (1), 20Ga–0Al (2), and 17.5Ga–2.5Al (3). The arrows indicate the position of Tg determined by the method of tangents. The heat treatment temperatures are indicated by the dashed lines.

Heating the glasses to approximately 40°C below the temperature of the onset of the exo-effect in the DSC curves makes it possible to obtain transparent glass-crystalline materials (GCM). The coefficient of their transmission near the maximum of the luminescence band (about 460 nm) is > 80% with sample thickness about 2 mm (Fig. 2). It is interesting to note that the introduction of Al_2O_3 significantly enlarges the temperature range where it is possible to obtain transparent GCM. Specifically, treatment of the glass 20Ga–2.5Al even at the temperature of the maximum of the exothermic peak (69°C) on the DSC curve does not result in significant reduction of the transmission coefficient, unlike the sample without Al_2O_3 (see Fig. 2). Moreover, a shift of the absorption edge in the UV region is fixed in the direction of shorter wavelengths on introduction of Al_2O_3 into the composition. Since this absorption in the heat-treated glass 20Ga–0Al is caused by the presence of the NC γ-Ga_2O_3, the observed shift is probably due to at least some of the aluminum ions entering into the structure of γ-Ga_2O_3. However, the scaling effect and the difference in the thermal past-history of these glasses cannot be completely ruled out [7].
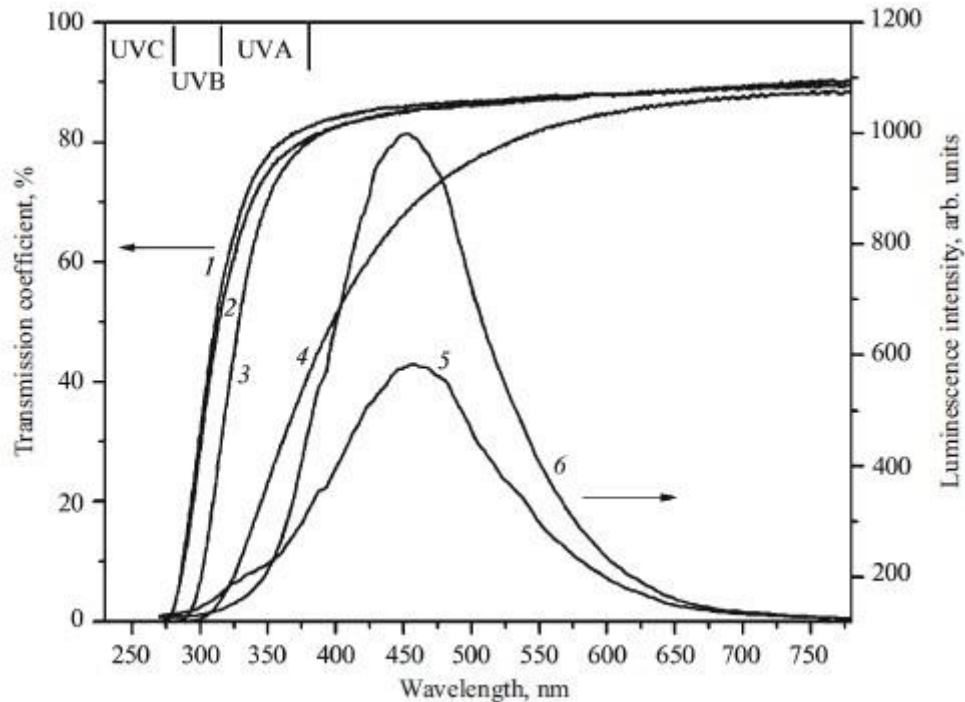
Fig. 2. Light attenuation and luminescence spectra (λexc = 250 nm, Δλexc = 4 nm, and Δλrec = 2 nm) of the treated glasses 20Ga–2.5Al (1, 2) 20Ga–0Al (3 – 6). The glasses were treated for 15 min at 691°C (2) or 675°C (4) as well as at 640°C (1, 3, 5, 6) using preliminary heating (3.5 h) at 615°C (1, 3, 6) or without it (5); UVC, UVB, and UVA— UV-radiation ranges.

In all glasses, according to XPA, γ-Ga2O3 precipitates as the primary crystalline phase. The size of the crystals does not exceed 10 nm, and the content of the crystalline phase for transparent samples reaches about 15%. These characteristics could not be determined for heat-treated (640°C, 15 min) glass 17.5Ga–2.5Al, whose crystallization power turned out to be lowest among the studied compositions. The introduction of Al2O3, as we expected, decreases the size of the precipitated NC, probably as a result of liquation temperature reduction and increase of the viscosity of the glass. Specifically, for heat treated (640°C, 15 min) glasses 20Ga–2.5Al and 20Ga–0Al the size of the crystals was equal to about 4.5 and 6 nm, respectively. The use of two-step heat-treatment results in further reduction of their size with a simultaneous small increase in the content of the crystalline phase. It should be noted that the estimate of the degree of crystallinity of the heat-treated glasses is correlated with data on the density of the same samples as determined by the hydrostatic weighing method.

Typical luminescence spectra for the example of the glass 20Ga–0Al, heat-treated in one- and two-step regimes, are presented in Fig. 2. The spectra are a superposition of UV blue and green bands, the ratio between which depends on the relative amounts of the intrinsic defects of the γ-Ga2O3 phase. Ordinarily, it is assumed that the oxygen vacancies act as donors, and the associates, formed owing to the strong electrostatic interaction of the cationic vacancies with oxygen vacancies, serve as acceptors [9].

The dependence of the integral intensity of the luminescence band on the NC concentration, calculated taking into account their size and crystallinity as well as the density of the GCM, is presented in Fig. 3. As the concentration increases, the intensity of the band, as a rule, increases, which is clearly seen in comparison with the glasses of the same composition which are heat-treated in different regimes, though some deviations are observed, owing to, aside from the size of the NC and the crystalline phase content, probably, other factors, for example, the composition of the NC. The use of pre-crystallization heat-treatment made it possible to appreciably increase the intensity of the band for all glasses, and for the sample of 20Ga–2.5Al heat-treated in one step this intensity is comparable with that for the other glasses treated in two steps. The maximum value of the intensity was achieved for GCM into whose composition Al2O3 was introduced above 100%. It should be noted that the two-step regime was chosen for the glass 20Ga–0Al and, evidently, it's not optimal for glasses with Al2O3, especially the composition 17.5Ga–2.5Al. The choice of heat treatment regime and the required amount of the additive Al2O3, undoubtedly, will increase the luminescence efficiency of the developed GCM.
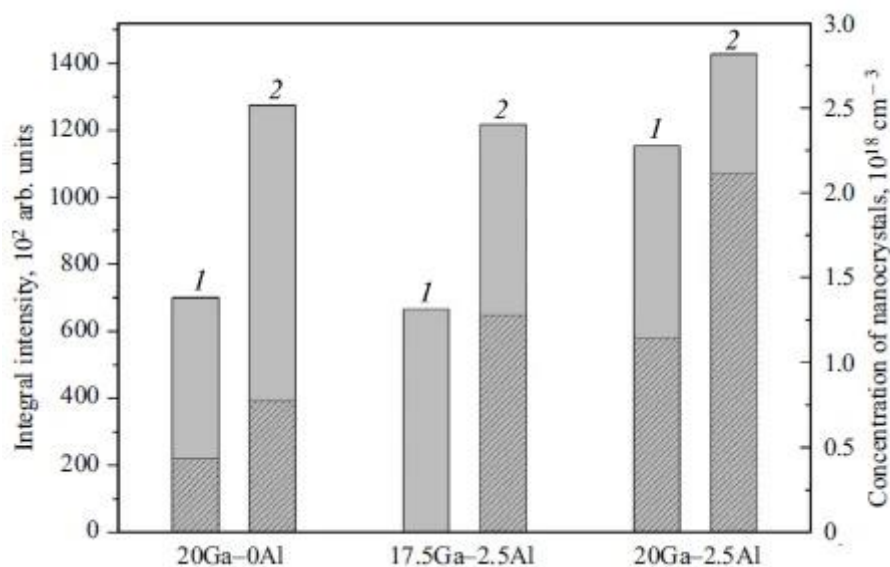

Fig. 3. Integral intensity of the luminescence band (gray columns) versus the concentration of nanocrystals (hatched part): 1) one-step treatment (640°C, 15 min); 2) two-step treatment (615°C, 3.5 h followed by 640°C, 15 min).

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