Секция 4. ОПТИКО-ЭЛЕКТРОННЫЕ СИСТЕМЫ, ЛАЗЕРНАЯ ТЕХНИКА И ТЕХНОЛОГИИ

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OPTICAL PROPERTIES OF SPINEL BASED GLASS-CERAMICS OF THE ZnO-Al_2O_3-Ga_2O_3-SiO_2 SYSTEM DOPED WITH Co^{2+} IONS

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Abstract. Transparent glass-ceramics containing Co^{2+}:$Zn(Al,Ga)_2O_4$ spinel nanocrystals with sizes of 6–11 nm were studied. Absorption band of the Co^{2+} ions in the material is shifted to longer wavelengths as compared with glass-ceramics with no Ga_2O_3 addition. Absorption saturation at 1.54 μm was observed and its characteristics (absorption recovery time, ground-state and excited-state absorption cross-sections) were measured. The developed glass-ceramics are promising as saturable absorbers for 1.6 μm erbium lasers.

Key words: transparent glass-ceramics; spinel nanocrystals; absorption saturation; cobalt ions; gallium oxide.

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Introduction. Materials doped with cobalt Co^{2+} ions placed in tetrahedral sites are well known as saturable absorbers for lasers emitting in 1.3–1.6 μm spectral region (see e.g. [1]). For this purpose saturation of absorption in the band related to the $^4A_2(^4F)\rightarrow{}^4T_1(^4F)$ transition of tetrahedrally coordinated Co^{2+} ions is used. Among such materials Co^{2+}:$MgAl_2O_4$ spinel single crystal is the most widely applied for passive Q-switching of erbium glass lasers emitting at 1.54 μm.

Spectral region of 1.5–1.7 μm attracts attention for range-finding, environmental sensing, telecom applications, etc. due to low propagation losses of light in the atmosphere and silica fiber. Several crystalline materials doped with Er^{3+} ions were recently developed as laser ones with emission wavelengths in the 1.6–1.7 μm spectral region (see e.g. [2]). For such lasers passive Q-switching with Co^{2+}:$MgAl_2O_4$ spinel single crystal is not very efficient. This is due to low absorption in the range of the $^4A_2(^4F)\rightarrow{}^4T_1(^4F)$ transition of Co^{2+} ions and consequently, low saturable absorption contrast at the lasing wavelength. Therefore, new materials containing Co^{2+} ions with high absorption in the range of 1.6–1.7 μm are needed.

Spectral properties of transition metal ions are sensitive to their surrounding, and this is used to adjust position of the absorption bands by designing the proper environment of the transition metal ion. Therefore, if the addition of gallium oxide (in our case) to the composition of the initial zinc aluminosilicate glass results in crystallization of the gallium-containing gahnite spinel, such material will provide a desired spectral shift of the Co^{2+} absorption band to longer wavelengths.

Samples Preparation. Initial glass of the composition 25 ZnO, 23 Al_2O_3, 2 Ga_2O_3, 50 SiO_2, (mol%) nucleated by 7 mol% TiO_2 and doped with 0.1 wt% CoO, both added above 100 % of the base composition, was prepared from the reagent grade raw materials. The glass was melted in a laboratory furnace with Globar heating elements at temperature T of 1580 °C for 6 h. Then the initial transparent violet-colored glass was cut into pieces and heat-treated in the muffle furnace by two-stage heat-treatments with the first hold at 720 °C and the second hold in the temperature range of 750–1000 °C. The structure of the initial glass and glass-ceramics was studied with X-ray diffraction (XRD) analysis (Fig. 1).

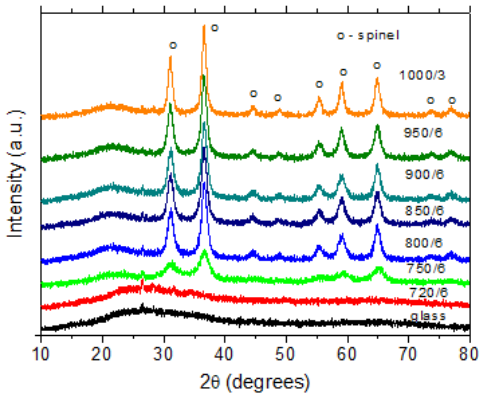

Figure 1 – XRD patterns of the initial glass and transparent glass-ceramics. *Labels* 750/6 – 1000/3 indicate the heat-treatment temperature, °C, and holding time, h, at the second stage, respectively. The nucleation stage is at 720 °C for 6 h. The patterns are shifted for the convenience of observation. *Circles* stand for the Zn(Al)Ga, $_2O_4$ spinel nanocrystals

The mean crystal sizes were estimated from the broadening of the X-ray peaks according to Scherrer's equation (1):

$$D = K\lambda/\Delta\cos\theta, \qquad (1)$$

where λ is the wavelength of the X-ray radiation (1.5406 Å), θ is the diffraction angle, Δ is the width of the XRD peak at half of its maximum, and K is the constant assumed to be 1 [30]. The size of spinel crystals was determined using the diffraction peak with the Miller indices (hkl) (440) at $2\theta \approx 65.5°$. The error in the mean crystal size estimation is about 5%.

Transparent glass-ceramics contained crystals of $Zn(Al_xGa_{1-x})_2O_4$ solid solutions with spinel structure with sizes of 6–11 nm and the lattice parameter a ranging from 8.107 to 8.130 Å. The zinc aluminogallate nanocrystals were homogeneously distributed within the highly silicate residual glass.

Luminescence. Luminescence spectra were registered after excitation made by filtered Xe-lamp irradiation at =512 nm. The relative error in determining the luminescence intensity was about 10 percent. Typical luminescence spectra are presented in Fig. 2.

The luminescence decay kinetics of samples was studied using an experimental setup based on a frequency doubled Nd^{3+}:$Y_3Al_5O_{12}$ laser with active Q-switching. The integrated luminescence signal in the range of 0.6–0.75 μm was recorded by photodetectors, the relative error was about 10 percent. Luminescence decay kinetics are presented in Fig. 3.

Absorption Saturation. Typical experimental data on initial absorption recovery after power light excitation demonstrates monoexponential nature with relaxation time $\tau = 790 \pm 10$ ns for the glass-ceramic prepared by heat-treatment at 1000 °C.

The experimental data on dependence of transmission of the glass-ceramics at $\lambda = 1.54$ μm on the input energy fluence was modelled with a slow saturable absorber model. This is due to the characteristic recovery time for Co^{2+} ions is few hundreds of ns (see e.g. [3]) that is much longer than the duration of the excitation pulse (70 ns in our case).

The best fitting curve results for ground-state absorption cross-section, σ_{GSA} are $(2.5–2.6)\times10^{-19}$ cm^2 for glass-ceramics prepared by the heat-treatment at 850 and 900 °C. The absorption saturation contrast, $\sigma_{GSA}/\sigma_{ESA}$ increases from 3 (for T = 800 °C) to 12.5 (for T = 1000 °C).

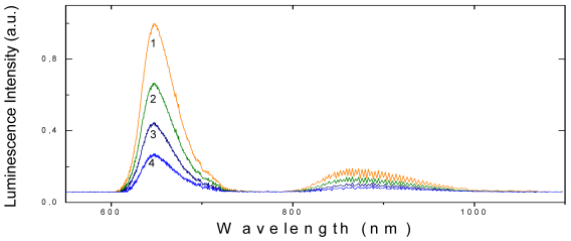

Figure 2 – Luminescence spectra of glass-ceramics prepared by heat-treatments at the second stage at: 1000 °C (1), 950 °C (2), 900 °C (3), 850 °C (4). The first stage is at 720 °C. The holding time at each stage except for 1000 °C is 6 h. The holding time at 1000 °C is 3 h. Excitation wavelength is λ = 532 nm

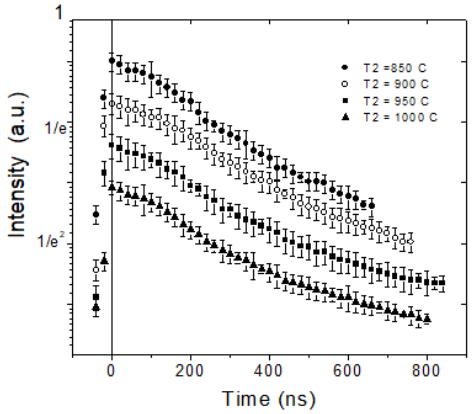

Figure 3 – Decay of the integral luminescence signal for the glass-ceramics. The first stage is at 720 °C. The holding time at each stage except for 1000 °C is 6 h. The holding time at 1000 °C is 3 h

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