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

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NON-LINEAR OPTICAL PROPERTIES OF TRANSPARENT GLASS-CERAMICS BASED ON Co^{2+}:$Zn(Al,Ga)_2O_4$ SPINEL NANOCRYSTALS

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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. The developed glass-ceramics is promising as saturable absorbers for 1.6 μm erbium lasers.

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

НЕЛИНЕЙНО-ОПТИЧЕСКИЕ СВОЙСТВА СИТАЛЛА, СОДЕРЖАЩЕГО НАНОКРИСТАЛЛЫ ШПИНЕЛИ Co^{2+}:$Zn(Al,Ga)_2O_4$

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Аннотация. В работе исследованы ситаллы, содержащие нанокристаллы шпинели состава Co^{2+}:$Zn(Al,Ga)_2O_4$ размером 6–11 нм. Полоса поглощения ионов кобальта в области 1,5 мкм в материале смещена на 20 нм в длинноволновую область в сравнении с ситаллами без добавления Ga_2O_3. На длине волны 1,54 мкм наблюдается насыщение поглощения под воздействием мощного оптического излучения. Исследованный материал перспективен для насыщающихся поглотителей лазеров на основе ионов Er^{3+} с длиной волны излучения в области 1,6 мкм.

Ключевые слова: ситалл; нанокристаллы шпинели; насыщение поглощения; ионы кобальта; оксид галлия.

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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, aerial navigation, telecom applications and laser surgery 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 [3]. Therefore, if the addition of gallium oxide to the composition of the initial zinc aluminosilicate glass result in crystallization of the gallium-doped spinel, such material will provide a desired spectral shift of the Co^{2+} absorption band used for Q-switching to longer wavelengths.

In this paper we present results of study of the new glass-ceramics of the zinc gallioaluminosilicate (ZGAS) system nucleated by TiO_2 and doped with CoO. The optical absorption and absorption saturation properties of these materials are reported below.

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 and 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 1580 °C. 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.

Fig. 1 shows the linear absorption spectra of the Co^{2+}-doped initial glass and glass-ceramics. The spectrum of the initial glass is a typical absorption spectrum of the Co^{2+} ions in aluminosilicate glasses [4]. Absorption spectra of glass-ceramics are characteristic for materials with tetrahedrally coordinated Co^{2+} ions, which can be confirmed by a comparison with absorption spectra of tetrahedral Co^{2+} ions in different single crystals (see, e.g. [5]).

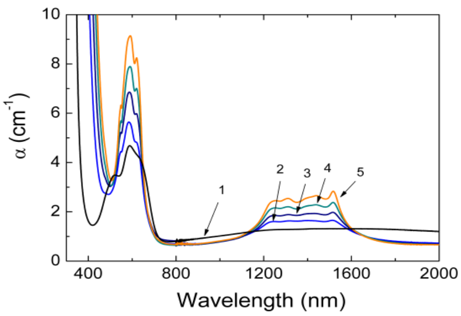

Figure 1 – Absorption spectra of the initial glass (1) and glass-ceramics prepared by heat-treatments at: 800 °C (2), 850 °C (3), 900 °C (4), 1000 °C (5)

Typical experimental data on initial absorption recovery after power light excitation are presented in Fig. 2. The relaxation demonstrates monoexponential nature. To evaluate the initial absorption recovery time τ, results were modeled using the dependence (1)

$$\Delta\alpha = A\exp(-t/\tau), \qquad (1)$$

where $\Delta\alpha = \alpha_0 - \alpha(t) = \ln(I(t)/I_0)$, α_0 – initial (non-excited) absorption coefficient, $I(t)$ – time dependent intensity of probing radiation transmitted through the sample, I_0 – initial intensity of probing radiation, A – numerical coefficient.

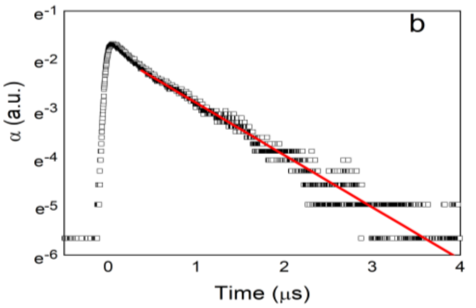

Figure 2 – Kinetics of relaxation of the bleached state for glass-ceramics prepared by heat-treatments at the second stage at 1000 °C

The measured relaxation time was τ = 790 ± 10 ns for the glass-ceramic prepared by heat-treatment at 1000 °C; τ = 815 ± 10 ns for the sample prepared by heat-treatment at 850 °C.

Fig. 3 presents transmission of the Co^{2+}-doped glass-ceramics as a function of input energy fluence at 1.54 mm wavelength, which corresponds to the $^4A_2(^4F)\rightarrow{}^4T_1(^4F)$ transition.

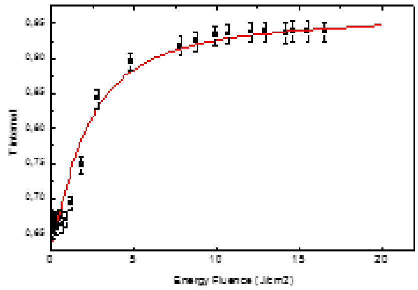

Figure 3 – Dependence of transmission of the glass-ceramics at λ = 1,54 μm on the input energy fluence

The experimental data were modelled with a slow saturable absorber model because the characteristic recovery time for Co^{2+} ions is few hundreds of ns that is much longer than the duration of the excitation pulse (70 ns in our case).

$$\frac{\mathrm{d}E}{\mathrm{d}z} = -h\nu\frac{\ln\left(\frac{1}{T_0}\right)}{L}(1-\gamma)\times \times\left(1-e^{-\frac{\sigma_{GSA}E}{h\nu}}\right)-\frac{\ln\left(\frac{1}{T_0}\right)}{L}\gamma E, \qquad (2)$$

where z denotes the axial coordinate inside the SA, $F_S = h\upsilon/\sigma_{GSA}$ is the energy absorption saturation fluence; h is the Planck constant; $\gamma = \sigma_{ESA}/\sigma_{GSA}$ is the absorption saturation contrast; σ_{ESA} and σ_{GSA} are the excited and ground state absorption cross-sections (ESA and GSA) for the SA, respectively.

The best fitting curve results are $(2.5–2.6)\cdot10^{-19}$ cm^2 for glass-ceramics prepared by the heat-treatment at 850 and 900 ºC. The absorption saturation contrast, γ^{-1}, increases from 3 (for T = 800 °C) to 12.5 (for T = 1000 °C).

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