Abstract—The fabrication technology of transparent Cr:LiGaSiO₄ nano-glass-ceramics was optimized after the investigation of the crystallization dynamics of Cr:Li-Ga-Si-O precursors. The samples with increased Cr⁴⁺ content are obtained.

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Cr⁴⁺ doped oxide materials attract a substantial attention as the active media of tunable and femtosecond solid-state lasers of the range 1.1-1.6 μm. Such lasers can be used in fiber optics communications, ophthalmology, laser ranging, etc. Cr⁴⁺ lasers can be pumped by commercial laser diodes emitting near 0.8 and 0.97 μm.

However, wide application of these lasers is suppressed by absence of really efficient hosts for this ion. Cr⁴⁺:Y₃Al₅O₁₂ and Cr⁴⁺:Mg₂SiO₄ single crystals, used in practice to the moment, have rather low fluorescence quantum yield and short excited state lifetime of Cr⁴⁺ due to strong non-radiative multiphonon relaxation. This leads to the enlarged thermal load of the active medium, and reduces the laser performance. Another problem is low available concentrations of Cr⁴⁺ and presence of the parasitic oxidation states of chromium in the above crystals.

The search of such hosts among single crystals and glasses during the last 25 years has not great success. At the last decade researchers pay much attention for another specific kind of optical materials, ultra-transparent nano-glass-ceramics as for the alternative hosts for Cr⁴⁺. Nano-glass-ceramics is the composite material consisting of a very fine crystallites (10-100 nm in size) distributed in the residual glass. These materials reproduce the valuable spectroscopic properties of the corresponding single crystals in substantial extent, but they can be rather easily obtained as high-quality samples of any shape (including single mode fiber waveguides) with high concentrations and uniform distribution of a dopant over the sample.

Earlier, we had studied the Cr:LiGaSiO₄ single crystals, which possess relatively high Cr⁴⁺ fluorescence quantum efficiency (~ 28%) and long lifetime (14 μsec). The structure of this crystal is favorable for Cr⁴⁺ formation, and unfavorable for the formation of Cr³⁺ and Cr⁵⁺. However, the incongruent melting of the compound prevents the possibility of growth of high-quality Cr:LiGaSiO₄ single crystals from melt. Therefore, last few years we are trying to develop an ultra-transparent nano-glass-ceramics of this composition.

In this talk we present the studies of different crystalline phases formation in the parent Cr:Li-Ga-Si-O glass depending on the temperature and duration of crystallization thermal treatment, as well as on the particular composition of the parent glass.

The vitreous precursors were fabricated by the standard melt- and quench technique. The partial controlled crystallization of the precursors was performed their two-stage annealing at special temperatures and durations. At the first stage the nucleation of the glasses performs, while at the second stage the growth of Cr:LiGaSiO₄ crystallites up to the desired sizes occurs. The 17 different compositions were tested during the work, including the stoichiometric Cr:LiGaSiO₄ composition, the ones with shifts from the stoichiometry into different directions, the samples with different chromium content, the partial substitution of a part of SiO₂ by GeO₂, or a part of Ga₂O₃ by Al₂O₃. Besides that, some modifying additions to the stoichiometric glass composition were tested (TiO₂, ZrO₂, BaO, WO₃, H₂BO₃). The temperatures providing the fastest nucleation were determined to be 550-600°C depending on the particular glass composition, whereas the temperatures providing the reasonable crystallization rates are 10-15°C higher.

We have also performed the studies of γ-LiGaSiO₄→α-LiGaSiO₄ crystallization dynamics at 800 °C, by the series of thermal treatments of the samples of different compositions. These studies allowed us to optimize the fabrication technology and to obtain the samples with the Cr⁴⁺ absorption coefficient of ~3.5 cm⁻¹ at pumping wavelengths, which exceed the best values for Cr:Mg,SiO₄ single crystals. The crystallization extent of the glass was evaluated to be ~ 50% in this case.