Synthesis and Luminescence of Fluorochloride Glasses Activated by Er$^{3+}$

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Abstract—Fluorochloride glasses activated by Er$^{3+}$ and glass ceramics of $57\text{HfF}_4 \cdot 20\text{BaCl}_2 \cdot 3\text{LaF}_3 \cdot 3\text{InF}_3 \cdot 17\text{NaF}$ composition were synthesized. For the given glasses, Er$^{3+}$ luminescence in the region of 1.55 µm was studied in comparison with fluoride glasses and glass ceramics of similar composition.

INTRODUCTION

Fluorozirconate glasses activated by rare earth elements are characterized by proper wide-ranged transmission and low relaxation losses. Such glasses are of interest for infrared laser fabrication, particularly of a mission and low relaxation losses. Such glasses are characterized by proper wide-ranged transmission of Er$^{3+}$, as well as in glass-ceramic samples produced by thermal treatment of these glasses.

EXPERIMENTAL AND RESULTS

Chemicals of 99.99% purity were used for synthesis of fluorochloride glasses. Glasses were fabricated in glass carbon crucibles at temperatures ranging from 830 to 840°C for 1.5 h in high-purity argon. Er$^{3+}$ concentration was varied within the limits of 1–8%.

It was found in experiments that the necessary condition for production of high optical quality glass is pre-

liminary thermal treatment of the initial barium chloride in chlorinating a medium like argon with addition of 3–5 vol % CCl$_4$ at a temperature of 780–800°C. Under these conditions, purification of barium chloride from oxygen-containing impurities occurs.

Samples for investigations of 4–5 mm in thickness were produced by casting of liquid melt into a brass mould with subsequent annealing at the glass-forming temperature. According to the data of X-ray spectrum analysis, the Cl-to-F atomic ratio in glasses, amounted to approximately 1/7, was slightly lower than this ratio in furnace feed (1/6 or 1/5); i.e., during synthesis, chlorine depletion of the melt occurred.

The produced glasses exhibited the following characteristics: the density was 5.85–5.90 g/cm$^3$, the refraction index was 1.515–1.517, and the infrared absorption edge was 8.2 µm.

Thermal treatment of the glasses was carried out in an interval from 10 min to 10 h in an inert atmosphere over the temperature range $t_x$–$t_y$ (see Fig. 1).

Depending on the temperature–time conditions, we obtained transparent, matt, and highly crystallized non-transparent glass-ceramic samples.

Crystallograms of fluorochloride glass ceramics indicate complex phase composition of highly crystallized glasses. Owing to the superposition of lines, X-ray identification of crystal phases segregated under thermal treatment is rather complex. Only crystal phase $\beta$-BaHf$_6$ has been reliably identified in highly crystallized nontransparent glass-ceramics.

Transmission spectra of glass of $57\text{HfF}_4 \cdot 20\text{BaCl}_2 \cdot 3\text{LaF}_3 \cdot 3\text{InF}_3 \cdot 17\text{NaF}$ composition doped with 1 at % Er$^{3+}$ and glass ceramics produced from such glass by means of its thermal treatment at a temperature of 305°C are measured in the visible spectrum region with an FDS-8 minispectrometer. Absorption bands characteristic of the Er$^{3+}$ ion are present in the spectra shown...
in Fig. 2. A distinctive feature of the transmission spectrum obtained for a glass-ceramic sample is a slight transmission decrease in the short-wave region of the spectrum, which probably is caused by light scattering on fine-grained crystalline particles.

Figure 3 displays the luminescence spectra of Er$^{3+}$ in the region of 1.55 $\mu$m in fluoride and fluorochloride glasses, as well as in fluoride and fluorochloride glass ceramics under excitation with a diode laser with $\lambda = 975$ nm.

Comparison of the shape of the spectra allows us to make the following conclusion. Chlorine insertion into the glass structure promotes a considerable shift of the luminescence line toward the long-wave region and small broadening of the line. It means that, in fluorochloride glasses, Er$^{3+}$ ions are characterized by mainly covalent bonds with dopants, and the long-wave shift is caused by the nepheloacoustic effect of the high-lying electronic states. The shape of luminescence lines in fluoride and fluorochloride glass ceramics is similar, which supposes the similarity of dopant fields in these materials. Crystallization of fluorochloride glasses leads to some shift of the luminescence lines toward the short-wave region, which can be explained by erbium displacement in a fluoride environment and dominating segregation of crystalline phases with a great degree of ionicity, especially barium fluorohafnates activated by erbium.

CONCLUSIONS

Fluorochloride glasses activated by Er$^{3+}$ of 57HfF$_4$ · 20BaCl$_2$ · 3LaF$_3$ · 3InF$_3$ · 17NaF composition and glass ceramics produced by thermal treatment of these glasses are synthesized.

X-ray investigations of Er$^{3+}$-doped glasses indicate a considerable difference in the luminescence characteristics of Er$^{3+}$ ions in fluoride and fluorochloride glasses and in glass ceramics. In particular, a pronounced change in position and width of the Er$^{3+}$ luminescence line in the region of 1.55 $\mu$m is observed.