Specific Features of the Formation of Oxyfluoride Glass-Ceramics in the SiO₂-PbF₂-CdF₂-ZnF₂-Al₂O₃-Er(Eu, Yb)F₃ System

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Abstract—Oxyfluoride glasses of the composition 0.3SiO₂⋅0.15AlO₃/₂⋅0.29–0.3CdF₂⋅0.18–0.3PbF₂⋅0.05ZnF₂⋅0.03Er(Eu, Yb)F₃ and the synthesis of the related glass-ceramic materials have been investigated. It has been demonstrated that heat treatment of the glasses is accompanied by the formation of a nanosized (16–25 nm) crystalline phase. X-ray powder diffraction analysis and measurement of spectral–luminescent characteristics have revealed that, during the phase decomposition induced in fluorosilicate glasses by rare-earth ions, these ions gradually pass from the vitreous matrix into nanocrystals of the cubic modification and form, hypothetically, the β-Pb₂₋ₓCdₓErₓF₃₋ₓ, crystalline phase, in which the value of x is constant and equal to 0.2, whereas the value of y varies from 0 to 0.145 depending on the composition of the initial mixture.

Key words: oxyfluoride glass-ceramics, IR and luminescence spectra, phase decomposition, nanocrystals
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INTRODUCTION
The development of the technology for manufacturing oxyfluoride glass-ceramics dates back to the 1970s. Auzel et al. [1] attempted to synthesize glasses that contained Ln₃O₅ (Y, La, Gd, Lu), Yb₂O₃, PbF₂, and Mn(O₄) (M = B, P, Te, Si, Ge) and were doped with Er₂O₃ or Tm₂O₃. As a result, they produced opaque glass-ceramic materials containing microcrystals with a radius of the order of 10 μm. The luminescence efficiency of these materials was higher than that of reference luminophors LaF₃ : Yb : Er by several factors. More recently, in 1993, Wang and Ohwaki [2] published the first work devoted to the synthesis of transparent glass-ceramic materials containing a cubic fluoride phase doped with erbium and ytterbium ions. These authors prepared materials that combined all advantages of the vitreous aluminoisilicate matrix and optical characteristics of low-phonon fluoride crystals. It is known that the most important problem in the design of transparent glass-ceramic materials, including those used for optical waveguides, is the minimization of light absorption and scattering losses. The Rayleigh scattering arising from microinhomogeneities with sizes close to the radiation wavelength is a constraining factor in the use of these materials and imposes strict limitations on the sizes of the precipitated crystalline phase. According to the concepts of the Rayleigh theory for the visible spectral range, the radius of crystals dispersed in the glass should be no larger than 15 nm. The difference between the refractive indices of the crystalline phase and the amorphous matrix should not exceed 0.1. Subsequently, these limitations were somewhat relaxed. In the framework of the model approach, Hopper [3] demonstrated the possibility of preparing transparent glass-ceramic materials with nanocrystals up to 30 nm in size and the difference between the refractive indices that does not exceed 0.3 [4]. Under specific conditions, even these mild limitations can be violated without detriment to optical characteristics of the material, which was confirmed for the glass-ceramic materials based on the SiO₂–Al₂O₃–MgO–ZrO₂–ZnO glass-forming system in which quartz crystals up to 10 μm in size precipitate [4].

Apart from the nanocrystal size, the shape of the formed nanocrystals is an important factor affecting the optical luminescence characteristics. Wang and Ohwaki [2] assumed that crystals of the β-PbF₂ type with sizes of the order of 20 nm precipitate in the system under consideration. Tick et al. [5] somewhat modified the composition used in [2] and synthesized the glass-ceramic material containing β-PbₓCd₁₋ₓF₂ nanocrystals with the refractive index n = 1.8, sizes of 9–18 nm, and a volume fraction of 15–30%.

Kawamoto et al. [6] investigated the optical characteristics of Er³⁺ ions in glasses and glass-ceramic materials with a close composition. It was assumed that the heat treatment initially leads to the precipitation of ErF₃ nanocrystals and then the shell of the β-PbₓCd₁₋ₓF₂ composition is formed on their surface.

Based on the electron microscopy data, Dejneka [7] discussed the mechanism of crystallization of the aforementioned oxyfluoride glasses subjected to different heat treatments. The inference was made that cubic nanocrystals of the simpler composition

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β-PbF$_2$: Er are formed in the system. In almost all more recent works [8, 9], the authors used the results obtained in [7] and considered β-PbF$_2$: Ln$^{3+}$ as the crystalline phase in glasses of the SiO$_2$–PbF$_2$–CdF$_2$–ZnF$_2$–Al$_2$O$_3$ system.

It should be noted that, according to the performed investigations, the introduction of rare-earth ions is a necessary condition for the manifestation of the low-temperature exothermic effect associated with the bulk crystallization in differential thermal analysis (DTA) curves.

In this work, we attempted to determine the possibility of preparing oxyfluoride glass-ceramic materials by varying the ratio between the contents of lead and cadmium fluorides and to analyze the crystallization products and the influence of the “glass–glass-ceramic material” transition on some physicochemical and spectral–luminescent properties.

**SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE**

Glasses of compositions 0.3SiO$_2$·0.15AlO$_{3.2}$·(0.29 – z)CdF$_2$·(0.18 + z)PbF$_2$·0.05ZnF$_2$·0.03Er(Eu, Yb)F$_3$ (where z = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.29) were synthesized using reagent-grade and special-purity grade reactants. A weighed portion was 50 g. The synthesis was performed for 30 min at $T = 1050^\circ$C in open corundum crucibles in air. The synthesis in the corundum crucibles made it possible to produce colorless glasses with a high transmission in the visible range. The glass melt was quenched between two cold glassy carbon plates. The quenched glasses had a thickness of no more than 2 mm and were annealed at a temperature of 30°C below the glass transition temperature $T_g$ in order to relieve residual stresses. With the aim of preparing glass-ceramic materials, the heat treatment was carried out at the temperature of the onset of crystallization, which was determined from the DTA curve. The differential thermal analysis was performed on a MOM Paulik-1500 derivatograph (Hungary). The thermal expansion was measured on a DKV-4 vertical differential quartz dilatometer, which provided the determination of the linear thermal expansion coefficient of materials with an error of no larger than 1.5 × 10$^{-7}$ K$^{-1}$. The sample was heated at a conventional rate of 5 K/min.

The luminescence spectra of the samples were recorded on an MDR-23 monochromator under excitation with a harmonic of an Ar laser (488 nm).

The IR absorption spectra were recorded on an IKS-21 spectrometer.

The X-ray diffraction patterns were measured on a Difrei diffractometer (Cu$K_\alpha$ radiation) with a bent coordinate detector in the range of 2$\theta$ angles from 16.4 to 59.7$^\circ$.

**RESULTS AND DISCUSSION**

In order to determine the temperatures optimum for precipitating the first crystalline phase and the tendency toward crystallization of glasses when introducing different rare-earth ions, we measured the DTA curves for the glasses containing 18 mol % PbF$_2$, 29 mol % CdF$_2$, and 3 mol % Er(Eu, Yb)F$_3$ (Fig. 1) and the glasses with a constant ErF$_3$ content (3 mol %) and different ratios between the cadmium and lead fluorides (Fig. 2). The analysis of the data obtained allowed us to make the following inferences (Table 1). The tendency toward crystallization increases in the order Yb–Er–Eu; in this case, the glass containing Yb at the temperature of the onset of crystallization ($470^\circ$C) does not crystallize for 5 h. As was previously shown by Beggiora et al. [12], the first exothermic effect (at ~520°C) corresponds to the bulk crystallization and second exothermic effect (at ~620°C) is associated with the surface crystallization. The analysis of the data presented in Fig. 2 makes it possible to draw the conclusion that an increase in the lead fluoride content results in a decrease in all characteristic temperatures (Tables 2, 3). No bulk crystallization is observed during the heat treatment of the glass containing 15 mol % PbF$_2$: both exothermic effects (at 560 and 620°C) correspond to the surface crystallization. An increase in the PbF$_2$ concentration to 18 mol %