Luminescent properties of Li_2O-K_2O-Al_2O_3-B_2O_3 glass-ceramics doped with Cr^{3+} ions

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***Abstract*— Li2O-K2O-Al2O3-B2O3 glass-ceramics doped with trivalent chromium ions was fabricated by melt-quenching technique. The glass-ceramics preparation process included 5 stages. The structure, optical and luminescent properties of glass-ceramics were investigated. The effect of Sb2O3with different concentration on structure and luminescent properties was carried out. It was demonstrated the introduction of antimony oxide leads to a shift of the maxima of exothermic transformations towards higher temperatures. The luminescence intensity of Cr3+ ions increased with increasing of Sb2O3. The maximum quantum yield was 44%, which confirms the possibility of using of glass-ceramics as active media in laser and fiber technologies, as well as for creating phosphor materials**

Keywords*— *alkali alumina-borate glass, glass-ceramics, luminescent properties, trivalent chromium ions

I. Introduction

Currently, technical progress in many industries, such as fiber and integrated optics, laser technology, information nanotechnologies, is mostly determined by the timely design of a material base, namely the synthesis and study of materials with pre-predicted properties. One of the most promising areas is the creation and study of glass-ceramics, such materials, where one or several crystalline phases are in the glass host. This is mainly due to the simple technology and the low synthesis cost, the possibility of flexible variation of characteristics. These materials combine the advantages of both crystals (small contribution of inhomogeneous broadening) and glasses (easy production). Crystal materials doped with chromium ions are intensively studied today [1]–[4]. The results of these studies of the spectral and luminescent properties of such materials are very optimistic: they have high cross-sections of stimulated emission radiation and big luminescence quantum yield. In this regard, they are often used as phosphor materials for red and white LEDs design [5].

Chromium ions can be in different valence states depending on their environment, while demonstrating different spectral properties. In many studies chromium ions with several valences are obtained during materials synthesis. Glass-ceramic materials activated by Cr^{4+} ions have a wide luminescence band in the near-IR spectral region, thereby they can be used as an active medium for tunable lasers in the 1.1-1.3 μm range. Materials doped with Cr^{3+} ions have intensive luminesce in the red spectral region [6], [7]. Over the past decades, interest in materials with a disordered structure doped with trivalent chromium ions has increased, as they can be used as materials for night vision devices [8], fiber optic thermal sensors [9], visualization [10] and photo catalysis [11]. It should be noted that, compared with crystals, the luminescence bands of amorphous materials have a rather large width and such materials have a low quantum yield [12], because of this their use in laser systems and phosphors is limited. Today, there is a solution to this problem - the nucleation of the nanocrystalline phase containing trivalent chromium ions in the glass host with high phase separation ability.

Therefore, this work is dedicated to the spectral and luminescent properties of aluminoborate glass-ceramics doped with chromium ions.

II. Material Synthesis

Glasses with host composition of 12.5 Li_2O-12.5 K_2O-25 Al_2O_3-50 B_2O_3 (mol%) were chosen as objects of study, in excess of 100% 0.1 mol% Cr_2O_3 and x mol% Sb_2O_3 (where x = 0, 2, 4) were introduced into the host (where x = 0, 2, 4). The synthesis was carried out in a Gero laboratory furnace in corundum crucibles at a temperature of 1400°C with stirring the melt with a platinum-rhodium stirrer in an oxygen atmosphere. Compared with previous works on glasses of aluminoborate system doped with chromium ions, iron [13] and copper [14], it was decided to introduce lithium oxide into the glass composition to increase the crystallization ability of glass host. It was shown in [15] that lithium tetraborate crystals are transparent in the visible and near IR ranges and can be doped with rare earth ions, including chromium.

The glass synthesis had five stages. During the first stage, a crucible (with an approximate capacity of 100 ml) was installed in a furnace and heated to 1400°C. After 10-minute delay backfilling started and lasted 60 minutes with 5 – 6 minute intervals. The second stage a total warm-up of the batch took place for 30 minutes after the end of the backfilling. The third stage was the stirring process with a platinum-rhodium stirrer with a rotation speed of 60 turns per minute, the duration of the stirring was 60 minutes. During the fourth stage after stopping the stirrer, the glass was maintained at a temperature of 1400 °C for 60 minutes to equalize the negative disturbance caused by the stirring and the removal of the stirrer. At the fifth stage, the crucible was taken out of the

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furnace, and the production of glass melt onto the metal mold took place.

III. Experimental Methods

The glass transition temperature was determined using a STA Jupiter 449 F1 differential scanning calorimeter from Netzsch. Measurements were performed at a heating rate of 10°C/min. A two-pass Lambda 650 Perkin Elmer spectrophotometer was used to obtain the absorption spectra in the wavelength range of 180–900 nm with the maximum optical density of 4.0. Plane-parallel polished plates of 1 mm thick were cut for the study. The Absolute PL Quantum Yield Measurement System (Hamamatsu) installation with an integrating sphere was used to measure the luminescence spectra, as well as to obtain the absolute luminescence quantum yield of the glass samples under study. The radiation source was a mercury-xenon lamp (Hamamatsu). All measurements were held at room temperature.

In this work, we used the X-ray diffractometer Ultima-IV (Rigaku). For the measurements, the radiation of the copper anode at a wavelength of 0.15418 nm was used. The angle resolution was 0.0001°. The mean crystal size was calculated from the width of the diffraction peaks (1):

$$D = k \cdot \lambda / (\Delta_{2\theta}) \cdot \cos\theta \qquad (1)$$

where D is the linear dimensions of crystals, λ is the X-ray wavelength, $\Delta_{2\theta}$ is the width of the diffraction reflection at half height, θ is the diffraction angle, and k is a constant, is taken to be unity [16].

IV. Experimental Results

Thermogram of glass with no Sb_2O_3 is shown in Fig. 1. A thermogram of glass absent of antimony oxide demonstrates the presence of a crystallization region with a maximum at a temperature of 603.9°C. The introduction of antimony oxide leads to a shift of the maxima of exothermic transformations towards higher temperatures. The glass transition temperature decreased down to 434°C and the crystallization peak temperature increased up to 608°C with the increase in antimony oxide concentration. Based on the data obtained, isothermal treatment of glasses was carried out at temperatures of about 600°C and above. This method was used for glass-ceramics synthesis.

Fig. 2 shows the absorption spectra of the glasses with different concentrations of antimony, which were obtained immediately after the synthesis. The graphs show the presence of two wide absorption bands in each glass, the first of which is located in the region of 620 nm, and the second is in the region of 420 nm. The long wavelength band is a typical absorption band of Cr^{3+} ions; it corresponds to the $^4A_2$ - $^4T_2$ transition [17]. The short wavelength band is due to the high-energy transition $^4A_2$ - $^4T_1$ of Cr^{3+} ions [17]. A band in the region of 350 nm corresponds to hexavalent chromium [18].

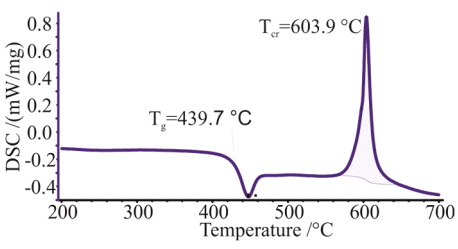

Fig. 1. Thermogram of the glass composition with 0 mol% Sb_2O_3

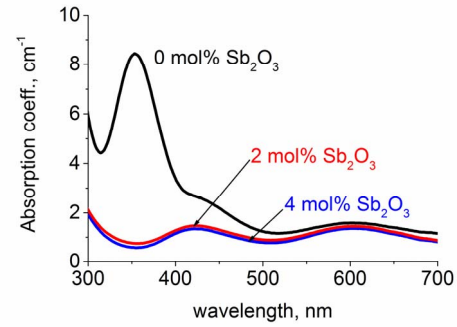

Fig. 2. Absorption spectra of the initial glasses

Fig. 3 shows the absorption spectra of glasses with different content of antimony oxide after the heat treatment at 630°C. The absorption bands underwent significant changes. The following tendencies can also be noted: distinct peaks in the 620 and 420 nm regions smoothed out, a small short-wave shift has occurred, total absorbance level increased, the relative intensity of the band at 350 nm has decreased.

Fig. 4 shows the luminescence spectra of glass-ceramics with different antimony oxide content under 500-nm excitation. The spectra show structural bands with a maximum in the region of 685, 700 and 715 nm. R-lines of bulk crystals doped with trivalent chromium [19] are located in the same region. This band corresponds to the transition from the excited ^2E state to the main $^4A_2$ [17] and corresponds to the case of a strong octahedral field, in which the ^2E level of Cr^{3+} is the energetically lowest radiative excited state [20]. Additional luminescent bands can be attributed to the Cr^{3+} luminescence in the low-symmetry environment (in amorphous glass host).

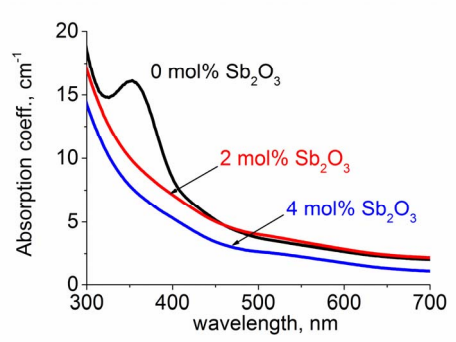

Fig. 3. Absorption spectra of the glasses heat-treated at 630°C

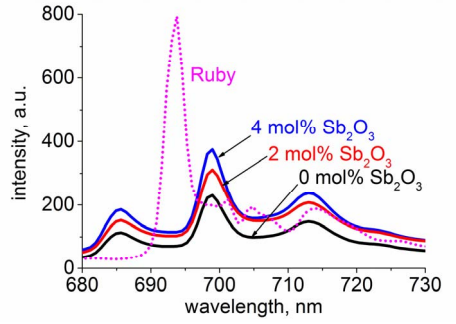

Fig. 4. Luminescence spectra of heat-treated glass samples and ruby crystal

Table 1 shows the luminescence quantum yield values of the glass-ceramics with different antimony oxide content

under excitation of 500 nm. It is seen that the quantum yield increases with an increase in the concentration of antimony oxide and with an increase in the heat treatment temperature. The quantum yield in this case depends on the fraction of chromium ions entering the crystalline phase in the total number of ions. The softening temperature of the glass-ceramics lies in the region of 630 – 650°C, because of this, the maximum heat treatment temperature was 700°C. A further increase in the temperature of isothermal treatment led to severe deformation of the samples and crystallization of lithium macrocrystals, due to which the glass-ceramics became opaque.

The X-ray diffraction pattern presented in Fig. 5 corresponds to the results of the X-ray diffraction study of glass-ceramic samples obtained at a temperature of 630 ºC. In Fig. 5, the most intense characteristic peaks are indicated for the crystalline phase. The location of the diffraction peaks was determined and the relative integrated intensity was calculated. Calculation of interplanar distances was made according to the Wulff-Bragg formula. Diffractograms of all glasses show the formation of $Li(Al_7B_4O_{17})$ nanocrystals. The size of nanocrystals was determined by the Scherrer formula (1) based on the location and intensity of the half-width of the diffraction maxima and was amounted to about 20 (± 1) nm for 600°C-heat treatment. After the samples undergo high-temperature heat treatment, the chemical composition of the crystalline phases is maintained with increasing average size.

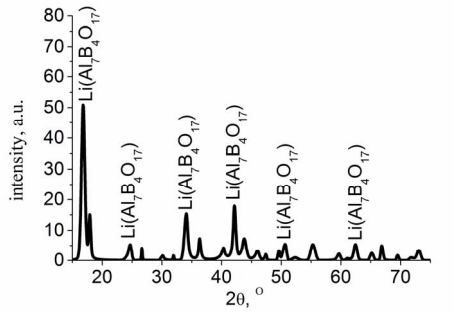

Fig. 5. X-ray diffraction pattern of the glass-ceramics obtained after the heat treatment at a temperature of 630ºC

TABLE I. INFLUENCE OF ANTIMONY OXIDE CONCENTRATION AND TEMPERATURE OF ISOTHERMAL TREATMENT ON THE LUMINESCENCE QUANTUM YIELD VALUES OF CHROMIUM IONS IN GLASS-CERAMICS

Sb_2O_3 content, mol%	Heat treatment temperature, °C	Quantum Yield, %
0	600	29.3
	630	34.7
	700	37.8
2	600	33.7
	630	34.8
	700	41.8
4	600	35.1
	630	43.1
	700	44.2

In the course of the work, aluminoborate glasses doped with chromium ions were synthesized. It was shown that when using an aluminoborate matrix doped with chromium ions, it was possible to obtain transparent glass-ceramics having an activated crystalline phase. Studies carried out by the DSC method showed the presence of one crystallization region. Isothermal treatment led to the growth of $Li(Al_7B_4O_{17})$ nanocrystals, which was confirmed by X-ray diffraction studies. The optical absorption and luminescence spectra of the obtained glass-ceramics contain bands corresponding to trivalent chromium ions similar to a ruby crystal. The maximum quantum yield was 44%, which confirms the possibility of using this material as active media in laser and fiber technologies, as well as for creating phosphor materials.

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