Crystallization kinetics and luminescent properties of chromium-doped borate glass-ceramics

A N Babkina, K S Zyryanova, D A Agafonova, R K Nuryev, E V Kolobkova and A I Ignatiev

Research Center for Optical Material Engineering, ITMO University, Birzhevaya line 4 199034, St. Petersburg, Russia

babkina.anastasya@bk.ru

Abstract. Chromium-doped alkali alumina borate glass was synthesized. The DSC studies exhibited glass transition temperature to be 425°C and glass crystallization temperature to locate in the 600–700°C range. After isothermal treatment of glass samples at temperatures from 540 to 700°C the chromium-doped borate glass-ceramics was obtained. The two bands of the glass absorption spectra shifted towards small wavelength region after the heat treatment with changing the glass colour. The XRD studies revealed the LiAl$_7$B$_4$O$_{17}$: Cr$^{3+}$ nanocrystals nucleation with the mean size of 12–25 nm. The glass-ceramics photoluminescence spectra possessed three intense bands in the 685–715 nm spectral region indicating high symmetrical environment around the chromium ions. The maximum value of the quantum yield was obtained after the heat treatment at 700°C was 50%.

1. Introduction

The laser generation was first obtained on a ruby crystal in 1960: T. Maiman showed a working model, which he had constructed in his research laboratory of Hughes, Malibu, USA [1]. The prerequisites for the laser creation were several theoretical and experimental studies related to spectral properties of ruby.

Ruby is a crystal of corundum, Al$_2$O$_3$, where a part of aluminum atoms is replaced by chromium atoms. If we talk about laser crystals, then, as a rule, chromium doping is 0.05 wt%, which corresponds approximately to the ion concentration of 1.6·10$^{19}$ cm$^{-3}$. Thereby corundum, which is usually colorless and transparent, acquires a pink color. Atoms of chromium, embedded in the crystal lattice, donate their three most weakly bound electrons to the external environment, as a result of which they become ions with a charge of 3$. They are responsible for the generation of laser radiation.

The ruby laser operation is based on a three-level scheme. At room temperatures only the lower $^4$A$_2$ level is populated, while others are almost unoccupied. In the first and following laser models, the pumping was carried out due to the broadband emission of the xenon flash lamp from the $^4$A$_2$ level to the $^4$T$_1$ and $^4$T$_2$ levels. These transitions are allowed transitions, due to the same spin and different electronic configurations of the states. The light is absorbed mostly in the violet (~ 410 nm) and green (~ 560 nm) regions. Nonradiative transitions between $^4$T$_1$, $^4$T$_2$ and $^2$E are the most likely, compared to direct transitions to the ground state. The lifetime at the $^4$T$_1$ and $^4$T$_2$ levels is very small, 5×10$^{-8}$ seconds, so when chromium atoms get to these levels, they quickly nonradiatively go to the $^2$A and E
sublevels of the \( ^2E \) level, which are the upper levels of the ruby laser, the laser generation occurs from them.

\( ^2E \rightarrow ^4A_2 \) transition is forbidden to spin and in the dipole approximation, because these level orbitals have the same configuration. Consequently, the \(^2E\) level is metastable, its lifetime is 3 ms. Thanks to this long lifetime it is possible to store considerable amount of energy, much greater than in the upper laser \(^4F_{3/2}\) level in the \( \text{Nd}^{3+} \) ion in \( \text{YAG:Nd}^{3+} \) lasers whose lifetime is about 0.25 ms. Big lifetime is the main advantage of the ruby laser, it allows to generate very powerful pulses in Q-switch mode.

Any of the \(^2A\) or \(E\) sublevels could be the upper level for the corresponding laser transition. But due to the rapid mutual relaxation \( (10^8\ s) \) thermal equilibrium is established for these levels, under such conditions the population of the \(^2A\) level is much lower than the \(E\) level. Because of this, laser generation occurs, as a rule, from the \(E\) state to the ground \(^4A_2\) state, which is usually denoted by \(R_1\). The wavelength corresponding to the transitions from the \(E\) level is 694.3 nm. However, conditions can be created for obtaining laser generation from the \(^2A\) - \(^4A_2\) transition with a wavelength of 692.9 nm. Such a transition is usually denoted by \(R_2\).

Crystalline materials activated by chromium ions are now being studied very intensively [2–4]. The results of the luminescent properties investigation of such materials are very optimistic: sufficiently high stimulated emission cross sections and a large quantum yield of luminescence have been obtained. In this regard, they are widely used as materials for designing of red phosphors and white light-emitting diodes [4]. Depending on their environment, the chromium ions can be in different valence states, demonstrating the difference in spectral properties. Glass-crystalline materials activated by \(\text{Cr}^{4+}\) ions have a broad luminescence band in the near-IR spectral region [5], which makes it possible to use them as an active medium for tunable lasers design in the range of 1.1-1.3 \(\mu\)m. The tuning range overlaps the second transparency window of the fiber optic communication line (1.3 \(\mu\)m) and is therefore of great practical interest. Amorphous materials activated by \(\text{Cr}^{3+}\) ions have intense luminescence in the red region of the spectrum [6,7]. Over the past decade, interest in the materials with a disordered structure activated by trivalent chromium ions has resumed in connection with the possibility of using such glasses as materials for night vision devices [8], fiber optic temperature sensors [9], visualization [10], and photo catalysis [11]. However, compared with single crystals, the luminescence of amorphous materials has a rather large width and low quantum yield [12], therefore their use in laser systems and for the creation of phosphors is limited. The solution to this problem is the nucleation of a nanocrystalline phase containing trivalent chromium ions in a matrix of glasses with high liquidation ability.

Owing to the presence of a large amount of alumina in the alkaline-alumina borate glass and the tendency of the alkaline-alumina borate matrix to liquation, it was proposed to dope the glasses with trivalent chromium ions for subsequent nucleation of a nanocrystalline phase containing chromium ions.

2. Experimental section

The object of research was alkaline-alumina borate glass, the matrix of which had the following composition: 12.5 \(\text{K}_2\text{O}-12.5 \ \text{Li}_2\text{O}-25\ \text{Al}_2\text{O}_3-50\ \text{B}_2\text{O}_3\) (mol%). Chromium was introduced into the glass matrix as a dopant in the form of oxide \(\text{Cr}_2\text{O}_3\) at a concentration of 0.1 mol% (over 100% of the matrix). Antimony oxide was also introduced into the glass to control the valence state of chromium. Previous studies have shown that chromium goes into a hexavalent state in glass that does not contain antimony oxide. We are interested in chromium in a trivalent state. Additives in the form of fluorine compounds ((\(\text{NH}_4\))\(\text{HF}_2\)) were introduced into the glass composition to improve the conditions of glass grid crystallization.

The synthesis of the initial glass was held in a laboratory high-temperature furnace (Gero) at a temperature of 1400 °C in corundum crucibles (about 100-200 ml volume). During the synthesis, the glass melt was mixed with a platinum-rod stirrer. The glass was annealed at a temperature of about...
350-400°C. The initial glass is green, optically transparent and homogeneous. Differential scanning calorimetry (DSC) was used to determine the glass transition temperature of experimental compositions and optimal temperatures for isothermal treatments of glasses. A STA 449F1 Jupiter (Netzsch) calorimeter was used to record DSC curves with a heating rate of 10°/min. Absorption spectra were recorded on a Lambda 650 spectrophotometer in the range of 300-850 nm, with a step of 0.1 nm and an integration time of 1 s. The absolute quantum yield and luminescence spectra were measured on an Absolute PL Quantum Yield Measurement System (Hamamatsu) experimental setup. Luminescence decay curves were measured by the standard facility, consisting of the radiation source, namely second harmonic of YAG:Nd\(^{3+}\) pulsed laser with a wavelength of 532 nm (Solar Laser Systems), 0.300 Meter Triple Grating Monochromator of 185-1100 nm range (Princeton Instruments), Si photodetector, Lock-In amplifier (Stanford research systems), and an Infinium 4-Channel Oscilloscope (Agilent).

X-ray diffraction patterns were obtained using an Rigaku Ultima IV X-ray diffractometer (Japan). The radiation of a copper anode with \(\lambda (\text{CuK}_\alpha) = 1.5418 \text{ Å}\) was used. Goniometer radius was 285 mm. The roentgenogram was taken in the range of angles 2θ/θ from 10° to 80° in the Bregg-Brentano geometry. Measurements were performed using a CuK\(_\beta\) filter. The scan rate at 2θ was 1°/min. The ICDD PDF-2 diffraction database (2008) was used to interpret diffraction reflections.

3. Results and discussion

The results of studies of the initial glass by the DSC method are presented in Figure 1. From Figure 1 it can be seen that the glass transition temperature is approximately 425°C (\(T_g\)). In the temperature range of 600–700°C, a big exothermic maximum is observed, which indicates the presence of bulk crystallization of the glass matrix at these temperatures. The peak of the exothermic region is located at 647°C (\(T_{cr}\)). Since chromium-containing nanocrystals should be obtained in glass by means of bulk crystallization, the optimum temperatures for carrying out isothermal treatments are temperatures in the range of 600-700°C.

![Figure 1. The DSC curve of the initial borate glass.](image)

The absorption spectra of the initial glass (Figure 2) contain two absorption bands in the region of 420 and 610 nm. Based on the literature data, in this area the absorption is found corresponding to transitions in the trivalent chromium ions \(^4A_2 - ^4F_1\) and \(^4A_2 - ^4F_2\) [13]. After heat treatment of the glass at a temperature of 600°C for one hour, the absorption bands are shifted to the short-wave region of the spectrum. In this case, the color of the glass changes from green to pink, and when irradiated with short-wave radiation, the glass acquires red luminescence.

Isothermal treatment at temperatures of less than 540°C does not lead to a significant change in the absorption spectra. As the isothermal treatment temperature rises up to \(T = 600°C\), the absorption bands begin to shift to the shortwave region up to 390 and 540 nm. With a further increase in
temperature, the intensity of the absorption bands increases together with an increase in the total scattering level of the glass matrix, so that after isothermal treatment at 700°C it becomes opaque.

![Figure 2](image1.png)  
**Figure 2.** Absorbance spectra of the initial borate glass (1) and the borate glass-ceramics after the heat treatment (2).

![Figure 3](image2.png)  
**Figure 3.** Photoluminescence spectra of the borate glass heat-treated at different temperatures.

On the luminescence spectra of glasses treated at temperatures above 540°C, there are three luminescence bands, located approximately in the region of 685, 700 and 715 nm. In this case, the band with a maximum at a wavelength of 715 nm has the form of a zero-phonon line band. Figure 3 shows that with an increase in the heat treatment temperature (for a duration of 1 hour) the intensity of the luminescence spectrum increases (the ordinate axis is presented in relative units). This is due to an increase in the intensity of absorption, namely an increase in the number of luminescent centers in the glass matrix. Due to the fact that the chromium concentration in glass samples is the same, different intensity and quantum yield (Figure 4) of luminescence can be associated with an increase in the proportion of chromium ions included in the crystalline phase. According to the literature, crystalline or glass-ceramic materials, in which chromium ions are in a highly-symmetric crystal environment, like ruby, alexandrite or spinel-based glass-ceramics, have similar luminescent characteristics [14,15].

![Figure 4](image3.png)  
**Figure 4.** Temperature dependence of the borate glass quantum yield (532 nm-excitation).

![Figure 5](image4.png)  
**Figure 5.** Temperature dependence of the luminescence decay time (532 nm-excitation).

The study of luminescent kinetic characteristics showed that the luminescence decay curves had two-exponential nature, consisting of a short and a long component. A short exponent has a decay time of about 1 millisecond, regardless of the glass treatment temperature. The decay time of the second
component increases with an increase in the heat treatment temperature (Figure 5). The two-exponential character of the luminescence decay curve is characteristic of many crystalline materials doped with trivalent chromium ions [16]. Commonly known that the first short component is responsible for transitions between the excited sublevels inside the $^2E$ level. The long component is directly responsible for the laser transitions (R1 or R2).

X-ray diffraction data show the nucleation in the glass matrix after the heat treatment of LiAl$_7$B$_4$O$_{17}$ crystals of the tetragonal system belonging to the I4/m space group. Chromium ions can be incorporated into the structure of these crystals, replacing aluminum ions (due to close ion radii). Thus, chromium ions incorporate into the crystalline environment of octahedral symmetry. With an increase in the heat treatment temperature, the mean crystal size, calculated using the Debye-Scherrer formula [17], increases from 12 to 25 nm. At the same time, in the temperature range from 600 to 700°C, it has almost no changes, however, the volume fraction of the crystalline phase in the material matrix increases from 50 to about 70%. This explains the loss of material transparency after the heat treatments at high temperatures. A further increase in the heat treatment temperature was meaningless, as it brought the material closer to the softening temperatures area.

Figure 6. The XRD data of the heat-treated samples of the borate glass.

4. Conclusion
As a result, chromium-doped alkali alumina borate glass was synthesized. The DSC studies exhibited glass transition temperature to be 425°C and glass crystallization temperature to locate in the 600 – 700°C range. After isothermal treatment of glass samples at temperatures from 540 to 700°C the chromium-doped borate glass-ceramics was obtained. The two bands of the glass absorption spectra shifted towards small wavelength region after the heat treatment with changing the glass color. The XRD studies revealed the LiAl$_7$B$_4$O$_{17}$: Cr$^{3+}$ nanocrystals nucleation with the mean size of 12 – 25 nm. The glass-ceramics photoluminescence spectra possessed three intense bands in the 685 – 715 nm spectral region indicating high symmetrical environment around the chromium ions. The maximum value of the quantum yield was obtained after the heat treatment at 700°C and was equal to 50%.

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