

# Synthesis and characterization of Cr<sup>4+</sup>-doped CaO–GeO<sub>2</sub>–Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>(Al<sub>2</sub>O<sub>3</sub>) transparent glass-ceramics

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## Abstract

Synthesis and devitrification behavior of Cr-doped CaO–GeO<sub>2</sub>–Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>(Al<sub>2</sub>O<sub>3</sub>) glasses have been studied. A range of glass compositions was found to yield transparent glass-ceramics after devitrification. The size of crystallites is below 1 μm. Glass-ceramic samples exhibit 1050–1600 nm broad-band emission with a maximum around 1260 nm, very similar to the emission of Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> bulk crystals. X-ray diffraction measurements indicate that the structure of crystallites exhibiting near infrared emission in glass-ceramics may be assigned to Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> with increased lattice parameters.

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## 1. Introduction

Study of the devitrification behavior of Cr-doped Ca(Mg)–Ge(Si)-based glasses is very important for the development of Cr<sup>4+</sup>-doped transparent glass-ceramics which may be used as a new material for optical communication applications, particularly optical fiber amplifiers. Transparent glass-ceramics containing nano-scale crystallites of proven Cr<sup>4+</sup>-doped laser materials may overcome the effects of non-radiative processes in Cr<sup>4+</sup>-doped glasses, because the optical properties of the glass-ceramics are expected to be similar to those of well developed bulk solid state laser materials, such as Cr<sup>4+</sup>:Mg<sub>2</sub>SiO<sub>4</sub> and Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> [1,2]. Recent progress on fiberization of glass-ceramic materials already has led demonstration of rare earth

doped fiber laser and amplifier with an efficiency uncompromised by the presence of crystals embedded within the core of the single mode fiber [3]. However, to date, properties of Cr<sup>4+</sup>-doped glass-ceramic systems have received little attention [4].

In this paper, synthesis of glasses characterized by volume crystallization of Cr<sup>4+</sup>-doped nano- and micro-size crystallites of calcium germanate in glass media during the post-fabrication heat treatment (devitrification) is described. The experimental work was focused on a search for melt compositions which yield glasses with desirable devitrification behavior.

Germanium-based glasses are characterized by anomalous behavior of various properties as a function of composition [5]. This is conjectured to be due to a change in co-ordination state of germanium with oxygen (tetrahedral GeO<sub>4</sub> to octahedral GeO<sub>6</sub>). The anomalies can be observed when the material consists not only of oxides of

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glass formers, but also of modifier oxides. Tetrahedrally and octahedrally co-ordinated germanate glasses are expected to provide favorable conditions for the stabilization of tetrahedral  $\text{Cr}^{4+}$  and octahedral  $\text{Cr}^{3+}$  optically active centers. Spectroscopic identification of  $\text{Cr}^{4+}$  and  $\text{Cr}^{3+}$  might be used as a test for Ge-co-ordination state in glass media.

It is known [5], that glass formation in the binary  $\text{CaO-GeO}_2$  system takes place only for  $\text{GeO}_2$ -enriched compositions. Approximate upper limit of calcium oxide in  $\text{CaO-GeO}_2$  system that participates in glass formation is about of 35 mol%. Devitrification of calcium tetragermanate,  $\text{CaGe}_2\text{O}_4$ , and calcium digermanate,  $\text{CaGe}_2\text{O}_5$ , glasses have been studied [6]. It was shown that the devitrification procedure produces  $\text{CaGe}_2\text{O}_5$  crystallites in the bulk, together with an unidentified crystalline phase in the calcium digermanate system, and only an unidentified crystalline phase in calcium tetragermanate.

To initiate crystallization of  $\text{Ca}_2\text{GeO}_4$  in glassy media, the glass composition should have the proper Ca/Ge ratio (at least two or higher). Boron oxide ( $\text{B}_2\text{O}_3$ ) was chosen as the basic glass-forming agent to be added to  $\text{CaO-GeO}_2$  system with the purpose to provide acceptable glass-forming ability of the system. Different modifiers were also used to assure volume formation of  $\text{Cr}^{4+}$ -doped micro/nano-crystallites in the glass media during devitrification.

## 2. Experimental procedure

### 2.1. Material synthesis and search procedure

To determine the glass-forming region, the samples were examined after quenching onto a metal plate. The resulting materials were obtained in three different states: glassy, partially crystalline (glass/polycrystal), and totally crystallized (polycrystal). These states were identified visually and by observation using an optical microscope. The 'glassy' state was used to delineate the glass-forming composition regions in the corresponding ternary system.

The search for glass compositions suitable for preparation of Cr-doped transparent glass-ceramics was carried out using simple procedure: producing glass slabs (melting ceramic batches, and quenching of the melt), devitrification of glass samples (heat-treatment at 450–550 °C to initiate crystallization in glass media), and testing fluorescence properties for the presence of Cr-based emission. Broad band emission centered at 900–950 nm was assigned to  $\text{Cr}^{3+}$  in octahedral co-ordination, and the band centered at 1200–1300 nm – to  $\text{Cr}^{4+}$  in tetrahedral occupation. The goal of this search procedure was to identify the glass compositions where volume crystallization of crystalline phase exhibiting  $\text{Cr}^{4+}$  fluorescence occurred.

Starting materials (reagent-grade  $\text{CaCO}_3$ ,  $\text{GeO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ ) were mixed in appropriate quantities to prepare batches of a size suitable to yield ~10 g glass samples. The batches were melted in an open Pt crucible in a

muffle furnace at 1400–1500 °C in air atmosphere. The furnace maintained temperature stability within  $\pm 1$  °C. The melt was quenched into a copper mold and annealed at 350–400 °C for 6 h to release thermal stresses. All glass compositions were doped by 0.5–1.0 wt%  $\text{Cr}_2\text{O}_3$  to reveal potential fluorescence properties of parent (as-quenched) glass and glass-ceramic samples.

### 2.2. Methods of characterization

X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and differential-thermal analysis (DTA) measurements were used to identify the structure of crystallites and characterize thermodynamic properties of glass and glass-ceramic samples. X-ray powder diffraction analysis was carried out using an automated Philips spectrometer ( $\text{CuK}\alpha$  radiation) with a graphite monochromator. TA Instruments (Model SDT 2960) was used for thermal measurements and analysis. DTA curves were recorded in air at 10 °C/min heating (cooling) rate on powder samples of approximately 30–70 mg of the powder in a Pt-cup in the 30–900 °C temperature range. The temperatures detected on the DTA curves are accurate to  $\pm 1$  °C.

Optical characterization of materials was carried out using Cary 500 spectrophotometer and a custom-made fluorescence measurement setup upon excitation by 680 nm laser diode. Fluorescence spectroscopy proved to be a very sensitive technique for the detection of the presence of  $\text{Cr}^{4+}$ -doped crystallites in glass-ceramics. The broad band fluorescence spectrum of tetravalent chromium (particularly for  $\text{Cr}^{4+}$ -doped  $\text{Ca}_2\text{GeO}_4$ ) typically located in wavelength range over 1  $\mu\text{m}$  is easily detected at even small amounts of crystallites in a sample.

## 3. Results

### 3.1. Glass-forming properties and devitrification behavior

After having tested numerous glass compositions, the glasses with the desired properties were discovered in the  $\text{CaO-GeO}_2\text{-Li}_2\text{O}_3\text{-B}_2\text{O}_3(\text{Al}_2\text{O}_3)$  system. The results on synthesis, devitrification behavior, and fluorescence properties of glasses and glass-ceramics are presented in Table 1. Molar value uncertainties in Table 1 are within  $\pm 0.01$ . All compositions were doped with 0.5–1.0 wt%  $\text{Cr}_2\text{O}_3$ . Experimentally determined glass-forming region in  $\text{Ca}_2\text{GeO}_4\text{-Li}_2\text{O-B}_2\text{O}_3$  pseudo-ternary system is shown in Fig. 1.

The initial set of experiments (#1–5, Table 1) were performed in the system  $\text{CaO-GeO}_2\text{-Li}_2\text{O-B}_2\text{O}_3$ . Compositions were varied within the area  $2.0\text{CaO-1.0GeO}_2\text{-(0.5-1.0)Li}_2\text{O}_3\text{-(0.34-0.78)B}_2\text{O}_3$ . Boron oxide is a key glass-forming component. Composition  $2.0\text{CaO-1.0GeO}_2\text{-0.7Li}_2\text{O}_3\text{0.34B}_2\text{O}_3$  (#5, Table 1) with low contents of  $\text{B}_2\text{O}_3$  was polycrystalline. Increasing the  $\text{B}_2\text{O}_3$  considerably improves glass-forming ability of the mixture. Good glass samples were obtained with compositions #1, 3, and 4 (Table 1). Lithium oxide usually acts as a network modifier

Table 1  
Glass compositions in CaO–GeO<sub>2</sub>–Li<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>(Al<sub>2</sub>O<sub>3</sub>) system

Exp. #	CaO Mol.	GeO <sub>2</sub> Mol.	Li <sub>2</sub> O Mol.	B <sub>2</sub> O <sub>3</sub> Mol.	Al <sub>2</sub> O <sub>3</sub> Mol.	Sample <sup>a</sup> 'as-quenched'	Sample <sup>b</sup> after devitrification	Fluorescence			
								Parent glass		Glass-ceramics	
								Cr <sup>3+</sup>	Cr <sup>4+</sup>	Cr <sup>3+</sup>	Cr <sup>4+</sup>
1	2.00	1.00	0.50	0.50	–	G	S/N	Yes	None	Yes	Yes
2	2.00	1.00	1.00	0.50	–	G/P	V/O	None	None	None	Yes
3	2.00	1.00	1.00	0.78	–	G	V/O	Yes	None	None	None
4	2.00	1.00	0.70	0.50	–	G	V/O	None	None	None	Yes
5	2.00	1.00	0.70	0.34	–	P	–	–	–	–	–
6	2.00	1.00	1.00	0.50	0.10	G	V/O	None	None	None	Yes
7	2.00	1.00	1.00	0.50	0.20	G	V/T	None	None	None	Yes
8	2.00	1.00	0.85	0.50	0.20	G	V/T	None	None	None	Yes
9	2.00	1.00	0.92	0.50	0.20	G	V/T	None	None	None	Yes

<sup>a</sup> G/P – glass/polycrystal, G – glass, P – polycrystal.

<sup>b</sup> S/N – surface crystallization, not-transparent; V/O – volume crystallization, opaque (semi-transparent); V/T – volume crystallization, transparent.

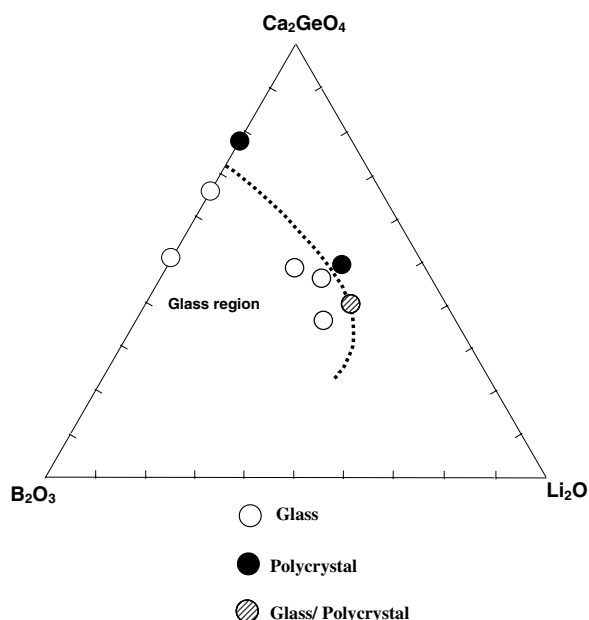


Fig. 1. Glass-forming region in Ca<sub>2</sub>GeO<sub>4</sub>–Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub> system.

[5], and increasing the content of Li<sub>2</sub>O in the CaO–GeO<sub>2</sub>–Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub> system changes devitrification behavior and degrades glass-forming ability. The composition with increased Li<sub>2</sub>O content (#2, Table 1) is characterized by poor glass-forming ability, and only a quarter of this batch was glass, and the rest was polycrystalline. Small amount of aluminum oxide improved glass-forming properties of CaO–GeO<sub>2</sub>–Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub> system (#6–9, Table 1). Aluminum may also act as a stabilizer for tetrahedral co-ordinated germanium [7] – the sites suitable for Cr<sup>4+</sup> substitution.

Test of emission properties of as-quenched (parent) glass revealed the presence of broad band fluorescence centered at 920 nm attributed to Cr<sup>3+</sup> in octahedral sites for two glass compositions, #1 and #3, both of them with increased B<sub>2</sub>O<sub>3</sub> contents. All other glasses did not exhibit any emission at room temperature. Testing emission properties of devitrified samples showed presence of broad-band emis-

sion centered at 1260 nm (Cr<sup>4+</sup> in tetrahedral occupation) for all compositions except composition #3 with increased contents of B<sub>2</sub>O<sub>3</sub>.

Heat-treatment procedure to initiate crystallization in glasses was carried out within the temperature range of 450–550 °C for different periods of time. As can be seen from Table 1, only the first composition with low content of Li<sub>2</sub>O (2.0CaO–1.0GeO<sub>2</sub>–0.5Li<sub>2</sub>O<sub>3</sub>–0.5B<sub>2</sub>O<sub>3</sub>) exhibited surface crystallization during devitrification. All other samples are characterized by volume crystallization. Adding 0.2 mol of Al<sub>2</sub>O<sub>3</sub> to the system radically changed crystallization behavior in glass media. Heat-treatment of Al<sub>2</sub>O<sub>3</sub>-containing samples (#7–9, Table 1) at 525 °C for 1 h yielded semi-transparent glass-ceramics with sub-micron size of crystallites. These compositions were used for more detailed examination. Fig. 2 shows optical microscopy image of the transparent glass-ceramic sample (composition #7, Table 1) exhibiting Cr<sup>4+</sup> emission (b), and parent glass sample (a). Parent glass did not exhibit any emission, but heat-treatment within the temperature range of 450–550 °C initiated nucleation of Cr<sup>4+</sup>-doped crystallites exhibiting NIR fluorescence.



Fig. 2. Optical microscopy picture of parent glass (a) and glass-ceramic (b) samples (glass composition #7, as-quenched and after heat-treatment at 525 °C for 1 h).

### 3.2. Material characterization

#### 3.2.1. Scanning electron microscopy (SEM) study

SEM was used to visualize crystallites formed during after-growth heat-treatment in glass media. Fig. 3 shows the scanning electron micrographs recorded for the fractured sample (#7, Table 1) after 1 h heat-treatment at 525 °C. The crystals formed in glass media after heat-treatment have spherulitic shape with the size up to 1 μm. We expect that crystallites with the size below 100 nm may be formed by adjustment of initial glass composition with nucleating agents and optimization of heat-treatment procedure parameters. The results of EDAX measurements to determine the chemical composition have shown approximately twice more atomic content of Ca compared with Ge in the crystallites, which corresponded to the  $\text{Ca}_2\text{GeO}_4$  chemical formula.

#### 3.2.2. Differential-thermal analysis (DTA)

DTA curves were recorded in air at 10 °C/min heating (cooling) rate on ~50 mg powder in a Pt-cup in the 30–1000 °C temperature range. The DTA curve (Fig. 4(a)) is typical for phase separated glass samples [8]. The curve exhibits a slope change in the 450–500 °C temperature

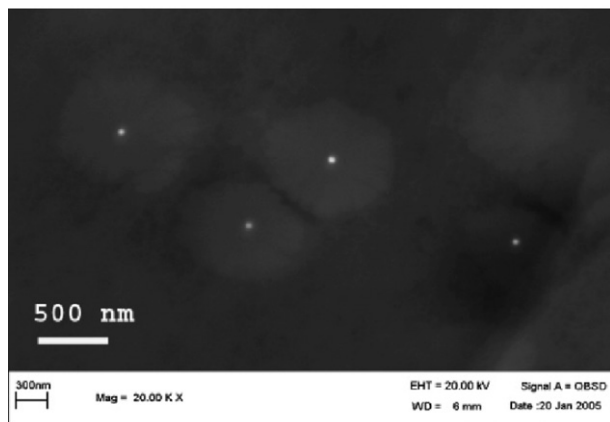
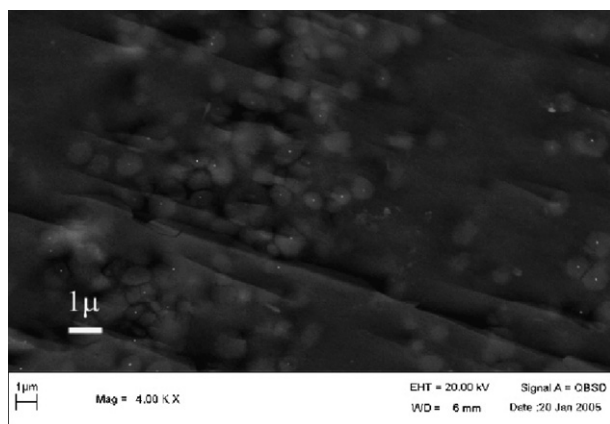


Fig. 3. SEM pictures of crystallites formed during after-growth heat-treatment (composition #7, 525 °C (1 h)).

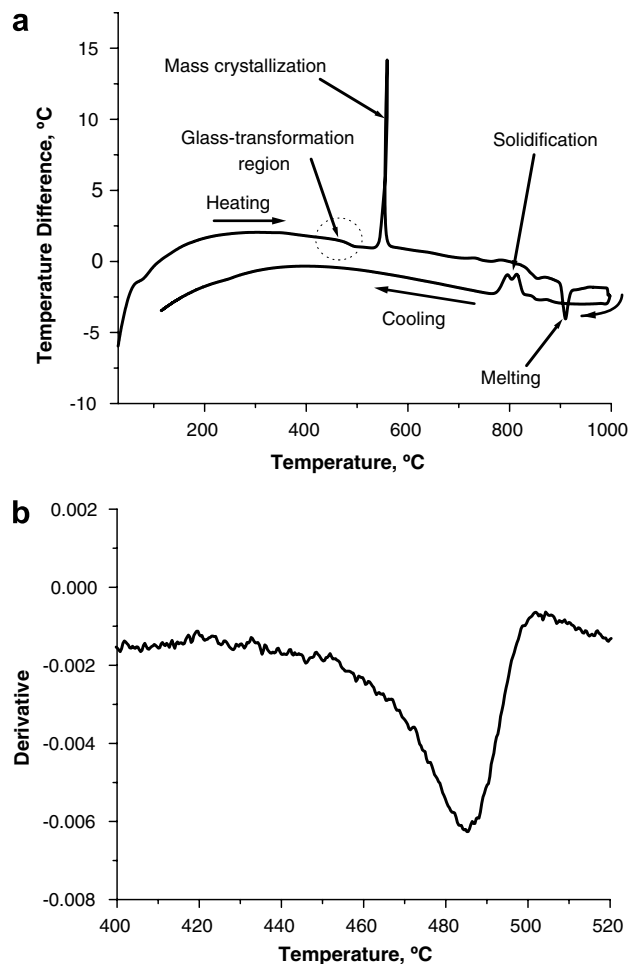


Fig. 4. Differential-thermal analysis results (a) with derivative plot (b) of glass transition region (composition #7).

range related to the glass transition. The inflection point at the slope change on the DTA curve at 485 °C (minimum on the derivative plot in Fig. 4(b)) is usually considered to be the glass transition temperature. The exothermic maximum at 560 °C corresponds to the separation of the crystalline phase. Crystallization starts at 540 °C (see onset of the maximum). Melting of the crystalline phase at a higher temperature appears as a minimum on the DTA curve at 908 °C. Cooling down of the sample without quenching leads to crystallization of the material at 800 °C.

#### 3.2.3. X-ray diffraction measurements

To identify the type of  $\text{Cr}^{4+}$ -doped crystals X-ray powder diffraction measurements have been carried out. All parent glasses were characterized by X-ray diffraction pattern without reflections. The appearance of X-ray diffraction reflections after devitrification is a firm evidence of crystal formation in the glass media.

Evolution of the crystalline phase in glass media during devitrification as a function of temperature and duration of heat-treatment is shown in Fig. 5 for composition #9. Heat-treatment at 475 °C for the period of 1 h leads to

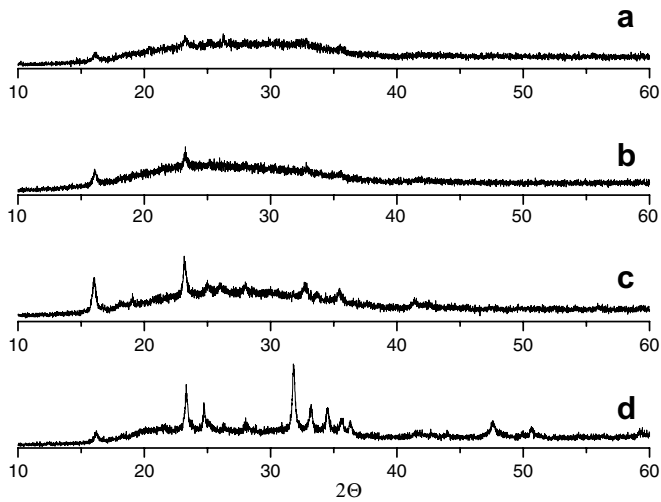


Fig. 5. X-ray diffraction spectra of  $2.0\text{CaO}-1.0\text{GeO}_2-0.92\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3-0.2\text{Al}_2\text{O}_3$  (#9, Table 1). (a) 460 °C (1 h); (b) 475 °C (1 h); (c) 490 °C (15 min); (d) 490 °C (1.5 h).

the appearance of first few reflections. Increasing the temperature and duration of heat-treatment leads to increased intensity of the reflections and appearance of new reflections.

X-ray diffraction spectra of glass-ceramics prepared from the parent glasses containing different amounts of  $\text{Li}_2\text{O}$ , and also with and without  $\text{Al}_2\text{O}_3$ , are characterized by similar reflections (Fig. 6). It means that there are no critical changes in crystalline structure of the crystallites formed during devitrification in that glass-ceramic composition range.

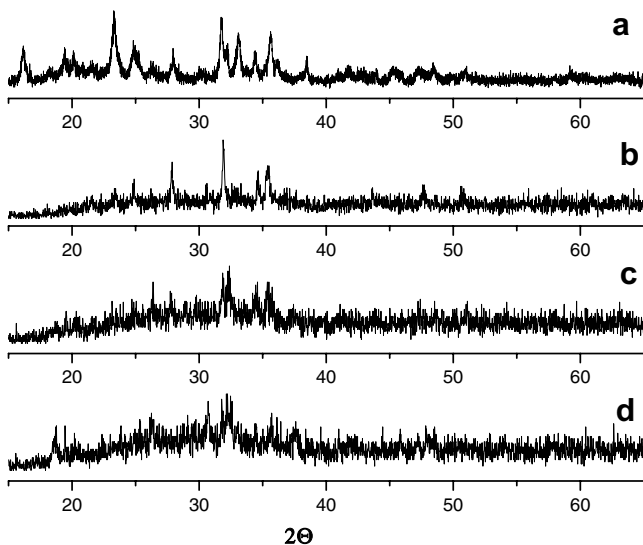


Fig. 6. X-ray diffraction spectra of glass-ceramic samples of different initial glass-composition (different  $\text{Li}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  contents). (a) #7 ( $2.0\text{CaO}-1.0\text{GeO}_2-1.0\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3-0.2\text{Al}_2\text{O}_3$ ); (b) #2 ( $2.0\text{CaO}-1.0\text{GeO}_2-1.0\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3$ ); (c) #4 ( $2.0\text{CaO}-1.0\text{GeO}_2-0.7\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3$ ); (d) #1 ( $2.0\text{CaO}-1.0\text{GeO}_2-0.5\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3$ ).

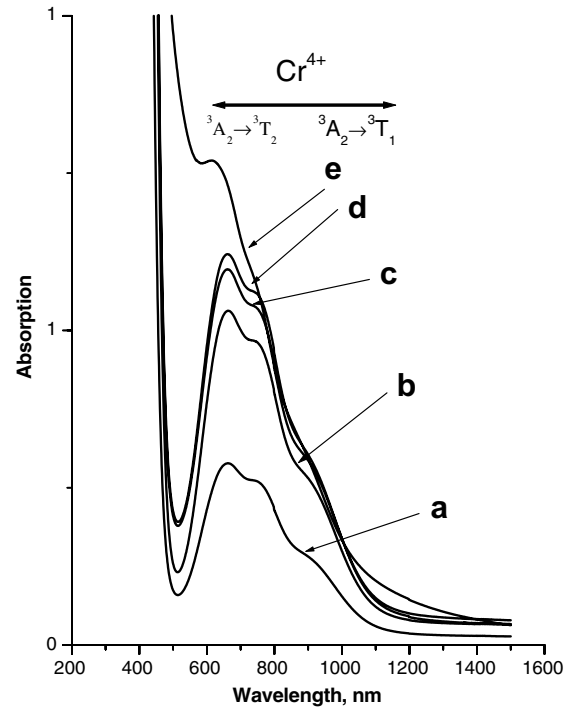


Fig. 7. Absorption spectra of  $2.0\text{CaO}-1.0\text{GeO}_2-0.92\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3-0.2\text{Al}_2\text{O}_3$  glass sample before heat-treatment and after different heat-treatment procedures: (a) parent glass, no heat-treatment, (b) 460 °C (1 h), (c) 475 °C (1 h), (d) 490 °C (15 min), (e) 490 °C (30 min).

### 3.2.4. Fluorescence and absorption measurements

Glasses of various compositions (Table 1) are characterized by similar absorption spectra with a maximum at  $\sim 660$  nm and a long tail extending beyond 1000 nm (Fig. 7, curve a). Long tail over 1000 nm in absorption is a feature commonly observed in  $\text{Cr}^{4+}$ -doped crystals. The absorption bands of  $\text{Cr}^{4+}$  located between 600 and 900 nm are usually attributed to  ${}^3\text{A}_2 \rightarrow {}^3\text{T}_1$  transitions and the weak near infrared absorption band around  $1 \mu\text{m}$  – to the  ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$  transitions. Similar spectra were observed in Cr-doped Ca–Al–Si–O glasses [9] where  $\text{Cr}^{4+}$ -oxidation state was achieved. Identification of Cr valence state in the parent glasses (before heat-treatment) by taking excitation emission spectra is difficult because of the prevailing non-radiative processes and lack of emission at room temperature.

Heat-treatment procedure and formation of crystallites in glass media does not essentially change absorption spectra except for the appearance of a background related to scattering off crystallites (Fig. 7). Light scattering significantly increases with the increasing temperature and duration of heat-treatment caused by the increasing size of crystallites.

Crystallization occurring in glasses during devitrification causes the appearance of emission in the 1000–1600 nm wavelength range with a maximum at about 1260 nm (Fig. 8). Increasing the temperature and duration of heat-treatment leads to increase of a number and size of crystallites that increase absorption of glass-ceramic media,



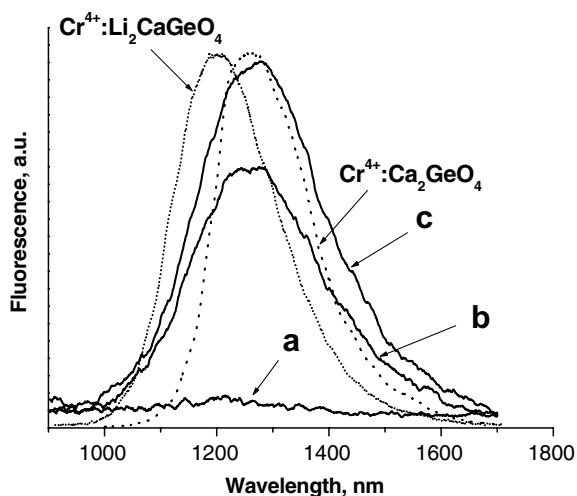


Fig. 8. Fluorescence spectra of glass-ceramic #9 ( $2.0\text{CaO}-1.0\text{GeO}_2-0.92\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3-0.2\text{Al}_2\text{O}_3$ ) after different heat-treatment procedures: (a) 490 °C (15 min), (b) 490 °C (30 min), (c) 490 °C (1.5 h), and fluorescence of  $\text{Cr}^{4+}:\text{Li}_2\text{CaGeO}_4$  and  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  reference samples.

and, as a result, the intensity of the fluorescence also increases, as shown in Fig. 8. Broad-band emission with a maximum around 1260 nm remains the same for all varieties of initial glass composition with different contents of  $\text{Li}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  shown in Table 1, which may confirm that the same type of crystallites is formed in these glasses after devitrification. The results of detailed spectroscopic study of Cr-doped  $\text{CaO}-\text{GeO}_2-\text{Li}_2\text{O}-\text{B}_2\text{O}_3(\text{Al}_2\text{O}_3)$  glass-ceramics will be published elsewhere.

#### 4. Discussion

Devitrification (heat-treatment) of glasses within  $2.0\text{CaO}-1.0\text{GeO}_2-(0.7-1.0)\text{Li}_2\text{O}_3-(0-0.2)\text{Al}_2\text{O}_3-0.5\text{B}_2\text{O}_3$  compositional range leads to volume formation of nano/micro-crystallites characterized by  $\text{Cr}^{4+}$  emission in the 1000–1600 nm wavelength range. Identification of crystallites formed in glass after devitrification was carried out using powder X-ray diffraction technique. Typical X-ray

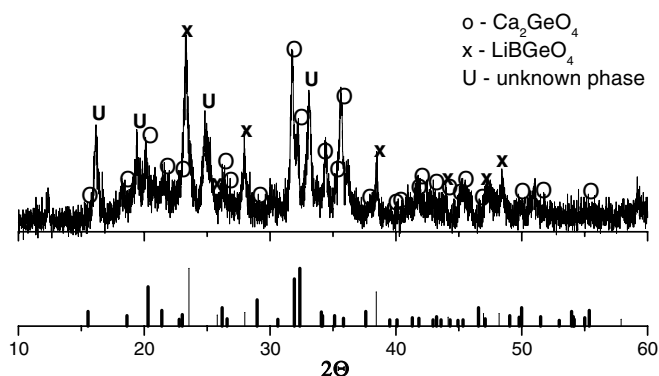


Fig. 9. X-ray diffraction pattern of glass-ceramic sample #7 ( $2.0\text{CaO}-1.0\text{GeO}_2-1.0\text{Li}_2\text{O}-0.5\text{B}_2\text{O}_3-0.2\text{Al}_2\text{O}_3$ ) and reference data (thick drop line –  $\text{Ca}_2\text{GeO}_4$  JCPDS #26-0304, and thin drop line –  $\text{LiBGeO}_4$  JCPDS #33-0792).

diffraction spectrum of glass-ceramic sample (composition #7 after heat-treatment at 525 °C for 1.5 h) is shown in Fig. 9. As can be seen from Fig. 9, two major crystalline phases may be identified as  $\text{LiBGeO}_4$  and  $\text{Ca}_2\text{GeO}_4$ . Some unknown XRD peaks are also present in the spectrum.

Additional data for identification of crystallites exhibiting near infrared emission may be acquired from the measurements of spectroscopic properties. Major feature of  $\text{Cr}^{4+}$  ions occupying tetrahedral sites in the crystal structure is a high probability of non-radiative transitions. For this reason the number of  $\text{Cr}^{4+}$ -doped materials exhibiting useful near infrared fluorescence at room temperature is very limited. Only three structural types of crystals with  $\text{Cr}^{4+}$  emission can be formed in the  $\text{CaO}-\text{GeO}_2-\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$  system:  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ ,  $\text{Cr}^{4+}:\text{Li}_2\text{CaGeO}_4$ , and  $\text{Cr}^{4+}:\text{LiAlO}_2$ . The latter one can be taken out of the consideration because Cr-doped glass-ceramic samples are also produced from the glass compositions without  $\text{Al}_2\text{O}_3$  (Table 1). Therefore, in order to make the structural identification of crystallites in glass-ceramics from spectroscopic data, only  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  and  $\text{Cr}^{4+}:\text{Li}_2\text{CaGeO}_4$  may be considered as a potential source of the near infrared fluorescence. However, X-ray powder diffraction reflections of  $\text{Li}_2\text{CaGeO}_4$  absolutely do not match reflections of glass-ceramics. As can be seen from Fig. 9, a number of XRD reflections of glass-ceramics including the maximal one at  $2\theta \sim 32^\circ$  may be assigned only to  $\text{Ca}_2\text{GeO}_4$  with increased lattice parameters. Therefore,  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystallites has to be considered as a sole source of fluorescence in glass-ceramics.

Fluorescence spectra of  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ ,  $\text{Cr}^{4+}:\text{Li}_2\text{CaGeO}_4$  and Cr-doped glass-ceramic samples are shown in Fig. 8. The maximum of the emission of  $\text{Cr}^{4+}:\text{Li}_2\text{CaGeO}_4$  is located at  $\sim 1180$  nm,  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  at  $\sim 1260$  nm, and Cr-doped glass-ceramics at  $\sim 1280$  nm. The spectrum of  $\text{Cr}^{4+}:\text{Li}_2\text{CaGeO}_4$  is characterized by a blue shift of about 100 nm with respect to the Cr-doped glass-ceramics spectrum. Spectrum of Cr-doped glass-ceramics is very similar to the spectrum of  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ , but slightly broader.

Taking into consideration the X-ray diffraction results and fluorescence spectra, formation of Cr-doped structurally distorted  $\text{Ca}_2\text{GeO}_4$  crystallites in glass-ceramics may be affirmed. The structure distortion could be caused by hetero-valence substitutions with Li or B occurring during the nucleation and growth of crystallites in solid state during devitrification.

#### 5. Conclusion

The glass-forming region and devitrification behavior of glasses in Cr-doped  $\text{CaO}-\text{GeO}_2-\text{Li}_2\text{O}-\text{B}_2\text{O}_3(\text{Al}_2\text{O}_3)$  system was studied. A number of glass compositions yielding transparent glass-ceramics after devitrification were found. The crystallite size is estimated to be less than 1  $\mu\text{m}$ . Glass-ceramic samples exhibit broad band emission in 1000–1600 nm wavelength range with a maximum around 1260 nm, very similar to  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  bulk crystals.

SEM, X-ray diffraction, and optical spectroscopy measurements were used to identify structure and chemical composition of crystallites. According to X-ray diffraction and optical spectroscopy measurements, the structure of the crystallites in these glass-ceramics is most likely a distorted  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  due to some isomorphous substitutions which occurred during the nucleation and growth of crystallites in glassy media during the devitrification. Adjustment of initial glass composition by adding nucleating agents and optimization of the heat-treatment procedure are expected to decrease the size of crystallites and improve the optical quality of glass-ceramic samples.

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