

**PRELIMINARY INVESTIGATIONS ON PREPARATION OF Ca_2GeO_4 AND $\text{Ca}_5\text{Ge}_3\text{O}_{11}$
GLASS-CERAMICS DOPED BY RARE EARTH IONS FOR LED APPLICATION
($\text{RE}^{3+} = \text{Tb}^{3+}$, Eu^{3+} AND Dy^{3+})**

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Abstract

Glasses with two different compositions doped by Tb^{3+} , Eu^{3+} , or Dy^{3+} ions were prepared from the oxide system $\text{CaO-GeO}_2\text{-Li}_2\text{O-B}_2\text{O}_3$. After thermal treatment Ca_2GeO_4 or $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ crystallize as a main phase. Thermal treatment conditions were determined from the DTA curves of the initial glasses. Excitation and emission spectra of the doped glass-ceramics contain the characteristic transitions of Eu^{3+} , Tb^{3+} , and Dy^{3+} ions. Some differences appear depending on the crystallizing phases. CIE coordinates of Eu^{3+} doped samples are placed in a very narrow area in the red part of the chromaticity diagram. CIE coordinates of the Tb^{3+} ion are more widely located in the green region. CIE coordinates of the Dy^{3+} ion are in a narrow area in the yellow chromaticity part. The studied glass-ceramics could be used as red, green, and yellow phosphors.

Keywords: Germanate phosphor, Rare-Earth doped glass-ceramics, Photoluminescence

1. INTRODUCTION

Light emitting diodes convert the electricity directly to light, so they appear as energy and environmental saving devices. The world energy consumption and harmful gas emission could be reduced by finding appropriate materials for LED application [1]. Such optical materials are widely used as sensors, solid state lasers, optical fibers in telecommunication, phosphors for displays and monitors [2]. Light emitting diodes allow controlled changes in spectral characteristics, which is an important quality for modern thin small size displays [3]. The luminescence of the rare earth activated phosphors depends strongly on the composition of the host, concentration of the activator, and methods of preparation [4].

Glass-ceramics combine the mechanical and optical properties of both glass and crystal. They are cheaper and easier for manufacturing compared with single crystals. Large size samples and higher doping concentrations can be achieved. Furthermore, particle size and the crystallization of the co-precipitate phases can be controlled by changing the thermal treatment conditions. The main disadvantage of glass-ceramics is that active ion generally is distributed between different crystallizing phases and the glass part in the sample [5].

Materials for light emitting diodes have to be chemical and physical stable, with strong absorption in the UV region, and high conversion efficiency [6, 7]. Inorganic oxide compounds are thermal, mechanical, and chemical stable, so they are promising as phosphor matrices. Different oxide compounds as tungstates, molybdates, phosphates, borates, silicates, germanates are investigated. The advantage of germanate compounds is their good luminescent characteristics. Furthermore, they are easy for preparing and possess more appropriate conductivity comparing with silicates. Therefore they are preferred in plasma and electroluminescent displays. Additionally, the germanate compounds show low thermal quenching, as opposite to molybdates and tungstates [9].

Alkali oxide borate glasses possess high electrical resistance and hardness, excellent chemical stability, and low melting temperature compared to silicate glasses [8]. Boron oxide becomes desired glass former, due to the higher length of the B-O bonds and boron's smaller cation size [10, 11]. The

presence of Li_2O in glass compositions is important because of its electrical conductivity and ion-exchange kinetics [9].

The two germanate compounds Ca_2GeO_4 and $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ possess different structures – orthorhombic and monoclinic. Calcium ions occupy different crystallographic positions; therefore the dopants could occupy different crystallographic sites in the lattice, which leads to different optical properties. As the ionic radii of Ca^{2+} and rare earth ions are close, the replacement of calcium is more likely [12].

Tb^{3+} , Eu^{3+} , and Dy^{3+} ions are well known for their luminescent properties [4, 13].

Tb^{3+} has a strong excitation band in the near UV region (around 380 nm) and emits green light (around 550 nm) because of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition. The intensity depends on the Tb^{3+} concentration. The emission from highly excited states can be observed in the blue part of the visible spectra when the concentration of the dopant is low. As human vision is most sensitive to green light, Tb^{3+} ion becomes more and more important [14]. Besides, Tb^{3+} ion can be co-doped with Eu^{3+} ion for obtaining of white light emitting medium [15].

Eu^{3+} has a strong excitation band in the near UV region (around 400 nm) and emits in the orange-red region (around 600 nm and in the range 610-630 nm) because of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions. The emission strongly depends on the matrix structure. The first one is stronger when the active ion is an inversion center. The latter is more intensive if the ion occupies the site without inversion symmetry. Eu^{3+} is important for obtaining white light through a combination in tricolor [4].

Dy^{3+} possesses a strong excitation band around 350 nm and emits two intensive lines – blue in the region 470-550 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition) and yellow in the region 570-600 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition). The latter transition is affected by local active ion surroundings. Dy^{3+} ion is of special interest because of the possibility to achieve white light in one host with single doping [13].

The first step in the process of glass-ceramics preparation is to find out the proper glass composition, where after devitrification the desire phase crystallizes. In addition, there are other requirements related to the glass such as homogenization temperature, evaporation, viscosity, etc. [16, 17].

Our previous investigations on the glass composition from the oxide system $\text{CaO-GeO}_2\text{-Li}_2\text{O-B}_2\text{O}_3$ allows us to select the most appropriate glasses for preparing glass-ceramics doped by rare earth activators [18]. The purpose of this study was to obtain glass-ceramics containing the RE^{3+} doped Ca_2GeO_4 , or $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ ($\text{RE}=\text{Eu}^{3+}$, Tb^{3+} , Dy^{3+}) and to investigate their optical properties. To our knowledge, these kinds of investigations are not published yet. The results are a part of a project, including photoluminescence properties investigations on solid state synthesized samples, glasses, glass-ceramics, and single crystals doped by Eu^{3+} , Tb^{3+} , or Dy^{3+} ions.

2. EXPERIMENTAL PART

CaCO_3 (p.a., Valerus), Li_2CO_3 (p.a., Valerus), GeO_2 (99.999%, Alfa Aesar), H_3BO_3 (p.a., Valerus), Eu_2O_3 (99.9%, Alfa Aesar), Tb_4O_7 (99.9%, Alfa Aesar) and Dy_2O_3 (99.9%, Alfa Aesar) was used as raw materials. Glass synthesis was carried out in a resistive furnace with Kantal heating wire permitted maximum working temperature of 1200°C and in a chamber furnace with MoSi_2 heating elements. The temperature was controlled with Pt/Pt–10%Rh thermocouple and Eurotherm controller. Glasses were melted in platinum crucibles in the air. First, the mixture was heated at 700°C for decomposition of the calcium carbonate, lithium carbonate, and boric acid and then the melt was heated at 1300°C for 3h for homogenization. As obtained melts were cooled down to room temperature by quick removing from the furnace and quenched by pouring onto a steel plate and pressing with another steel plate.

Different thermal analyses were done on the DTA/TG device of SETARAM, France. The samples were investigated at a heating rate of 10 °C/min in air flow at a flow rate of 20 ml/min.

The prepared glasses were thermally treated for establishing the crystallizing phases. The thermal treatment conditions are chosen on the basis of DTA analyzes.

Structural characterization was carried out by powder X-ray diffraction using a Bruker D8 Advance powder diffractometer with Cu K α radiation and a SolX detector. X-ray diffractograms were recorded at room temperature. Data were collected in the 2 θ range from 10 to 80° with a step 0.04° and 1 s step⁻¹ counting time. X-ray diffractograms were identified using the Diffractplus EVA program [19, 20].

The emission and excitation spectra were measured on Horiba Fluorolog 3-22 TCS spectrophotometer equipped with a 450 W Xenon Lamp as the excitation source. All spectra were measured at room temperature.

3. RESULTS AND DISCUSSION

Homogeneous glasses were obtained after melting at 1300°C and holding during 3 hours. Higher temperatures are not recommended because of the evaporation of the Li₂O, B₂O₃ and GeO₂. Figure 1 displays the chosen glass compositions for glass-ceramic preparation from the phase diagram CaO-GeO₂-LiBO₂ (Li₂O:B₂O₃=1:1). The four-component phase diagram can be represented as three-component diagram holding two of the components in the same molar ratio.

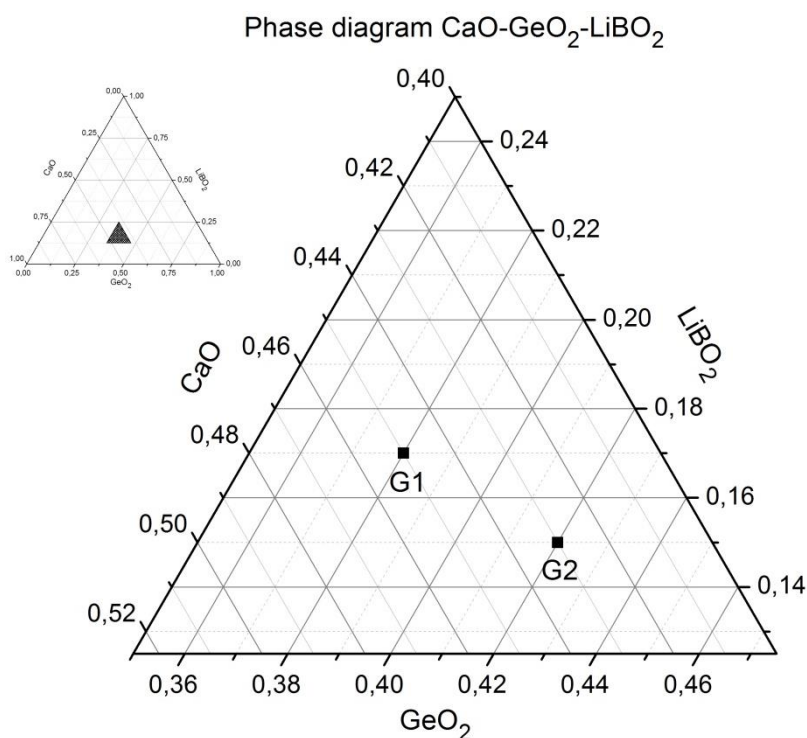


Fig. 1. Glass compositions for glass-ceramic preparation in the phase diagram CaO-GeO₂-LiBO₂ (Li₂O:B₂O₃=1:1).

The glass compositions from the oxide system CaO-GeO₂-Li₂O-B₂O₃, concentrations of Tb³⁺, Eu³⁺ and Dy³⁺ ions in the glasses, thermal treatment regime, and the crystallizing phases in the glass-ceramics after thermal treatment are summarized in Table 1. The RE³⁺ concentrations are calculated relative to the Ca²⁺ concentration without reducing the Ca²⁺ in the glass. The ionic radii of RE³⁺ in different coordination (Tb(VI) – 0.923 Å, Eu(VI) – 0.947 Å, Dy(VI) – 0.912 Å, Tb(VII) – 0.98 Å, Eu(VII) – 1.01 Å, Dy(VII) – 0.97 Å) are closed to that of Ca²⁺ (Ca(VI) – 0.99 Å, Ca(VII) – 1.06 Å) and very different from that of Ge(VI) – 0.53 Å and Li(VI) – 0.76 Å, so it is expected that the Rare earth ion would prefer to substitute the calcium ion in the crystal lattice in the glass-ceramic nano-particles [12]. The rare earth concentrations are chosen based on our previous investigations [21-23]. The thermal

treatment regime is based on DTA analyzes, presented in Table 2. As it is seen, the glass with composition G2 is more stable because of the higher glass stability parameter Tx-Tg.

Glass	CaO	GeO ₂	LiBO ₂	Tb ³⁺ [at%]	Eu ³⁺ [at%]	Dy ³⁺ [at%]	Thermal treatment regime	Crystallizing phases
G1	45	38	17	2	3	1	620°C, 2 h	Ca ₂ GeO ₄ + unknown phase
G2	43	42	15	4	3	4	620°C, 4 h; 700°C, 3 h	Ca ₅ Ge ₃ O ₁₁ + Li ₂ GeO ₃

Table 1. Glass compositions from the oxide system CaO-GeO₂-Li₂O-B₂O₃, concentrations of Tb³⁺, Eu³⁺ and Dy³⁺ ions in the glasses, thermal treatment regime and crystallizing phases after thermal treatment.

Glass composition		Dopant concentration [at. %]	Tg [°C]	Tx [°C]	Tc [°C]	Tx-Tg [°C]
G1	Non-doped	0	526	584	671	58
		2	527	581	677	54
	Tb ³⁺	3	536	600	679	64
	Eu ³⁺	1	530	585	675	55
	Dy ³⁺					
G2	Non-doped	0	517	634	657	117
		4	512	638	652	126
	Tb ³⁺	3	516	640	658	124
	Eu ³⁺	4	535	660	678	125
	Dy ³⁺					

Table 2. DTA data of the investigated glasses (Glass transition temperature Tg, Crystallization onset Tx, Crystallization temperature Tc and Glass stability parameter Tx-Tg)

In all glass-ceramics additional phases also crystalize. Figure 2 shows the XRD patterns of crystallizing phases in the glass-ceramics, where Ca₂GeO₄ or Ca₅Ge₃O₁₁ presents.

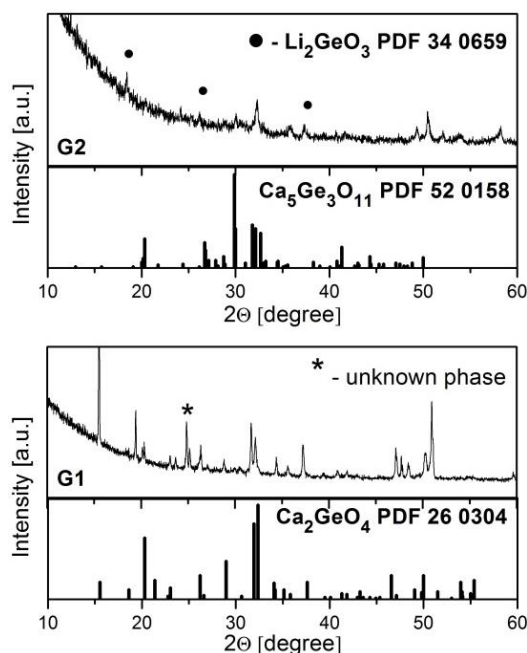


Fig. 2. XRD patterns of crystallizing phases in the glass-ceramics.

In glass composition G1 in addition to Ca_2GeO_4 unknown compound crystallizes. This phase is defined as base-centered orthorhombic with space group C2221, and cell parameters $a=9.1430$ Å, $b=9.1430$ Å and $c=7.1620$ Å. Details on its structure will be published elsewhere. In glass composition G2 together with $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ crystallizes Li_2GeO_3 as an additional phase.

Tb^{3+} doped glass-ceramic excitation and emission spectra are presented in Figure 3.

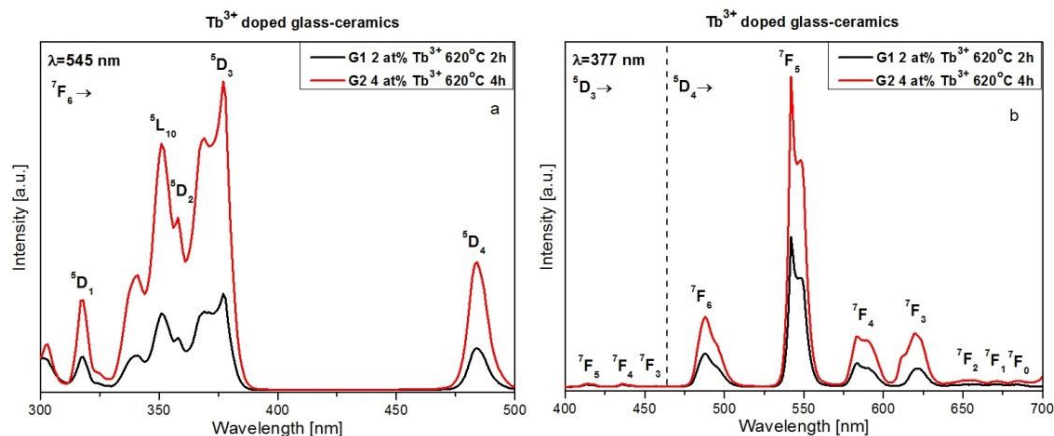


Fig. 3. Tb^{3+} doped glass-ceramic a) excitation and b) emission spectra

Tb^{3+} doped excitation spectra of the glass-ceramics in the range 300-500 nm, monitored at 545 nm, consist of the characteristic peaks of Tb^{3+} ion in this range and do not show significant differences. The highest peak is located at 377 nm corresponding to the ${}^7\text{F}_6 \rightarrow {}^5\text{D}_3$ transition. Other peaks are located at 303 nm (${}^7\text{F}_6 \rightarrow {}^5\text{H}_5$), 317 nm (${}^7\text{F}_6 \rightarrow {}^5\text{H}_7$), 351 nm (${}^7\text{F}_6 \rightarrow {}^5\text{D}_2$), 358 nm (${}^7\text{F}_6 \rightarrow {}^5\text{L}_{10}$) and 483 nm (${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$) [24]. Emission spectra in the range 400-720 nm, monitored at 377 nm excitation, also consist of the Tb^{3+} ion characteristic peaks. According to Aspinall [25] and Ligner [26], ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transitions in the emission spectra are sensitive to the active ion environment and the

$^5D_4 \rightarrow ^7F_3$ transition displays strong optical activity. As can be seen, these transitions are split in both glass-ceramic samples. It was mentioned above, that glass-ceramics contain crystalline and glassy parts. Probably this is the reason for the splitting of the peaks in the emission spectra because the active ion is distributed between the glass and the crystals. In addition, there are two crystallizing phases in the crystalline part of the samples.

Eu³⁺ doped glass-ceramic excitation and emission spectra are presented in Figure 4.

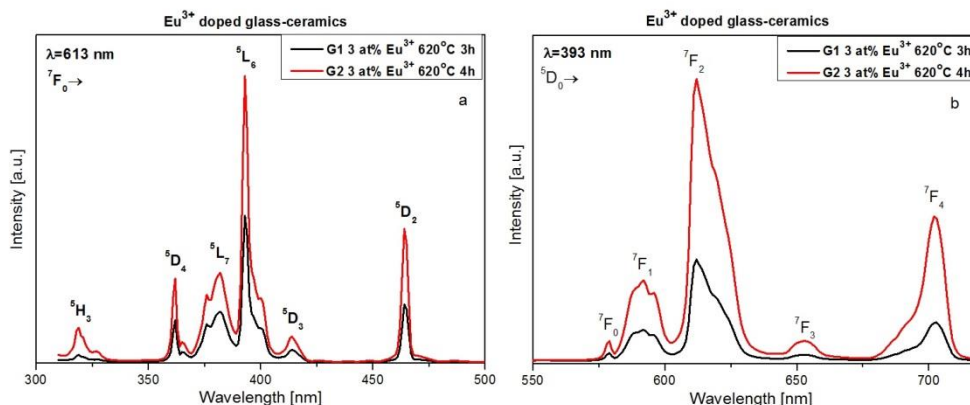


Fig. 4. Eu³⁺ doped glass-ceramic a) excitation and b) emission spectra

The excitation spectra of Eu³⁺ doped glass-ceramic monitored at 613 nm in the range 310-500 nm consist of characteristic peaks of Eu³⁺ ion [4, 24]. The transition with the strongest intensity is located at 393 nm (caused by the $^7F_0 \rightarrow ^5L_6$ transition). Other transitions are located at 318 nm ($^7F_0 \rightarrow ^5H_3$), 362 nm ($^7F_0 \rightarrow ^5D_4$), 382 nm ($^7F_0 \rightarrow ^5L_7$), 414 nm ($^7F_0 \rightarrow ^5D_3$) and 464 nm ($^7F_0 \rightarrow ^5D_2$). Emission spectra in the range 550-720 nm, monitored at 393 nm excitation also consist of the Eu³⁺ ion characteristic peaks, caused by $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, $^5D_0 \rightarrow ^7F_4$ transitions. The experimental data are in good agreement with Eu³⁺ transitions observed from other authors [27-29]. Some differences are observed in the spectra depending on the glass-ceramic composition. The transition $^5D_0 \rightarrow ^7F_0$ in the Eu³⁺ luminescence spectrum does not degenerate. If more than one peak appears, then more than one surrounding of the active ion is presented [25]. Peak analyses in the range 550-675 nm show that a weak shoulder appears for $^5D_0 \rightarrow ^7F_0$ transition at 577 nm into the peak at 579 nm, which is more prominent in the G2 glass-ceramic spectrum. The splitting of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions and the F2/F1 ratio provides information on the symmetry around the Eu³⁺ ion [4, 27, 30]. The peak for $^5D_0 \rightarrow ^7F_1$ transition is a three-fold split and the peak for $^5D_0 \rightarrow ^7F_2$ transition is a two-fold split. This result also confirms the presence of more than one environment of the Eu³⁺ ions. The F2/F1 ratios for G1 and G2 compositions are 3.34 and 3.66 respectively. Therefore the crystallites in glass-ceramic with composition G1, where Ca₂GeO₄ crystallizes, are with higher symmetry. The peaks at 703 nm, corresponding to the $^5D_0 \rightarrow ^7F_4$ transition, are also split. As an electric dipole transition, it is sensitive to the Eu³⁺ environment, but also the chemical composition [30].

Figure 5 presents Eu³⁺ doped glass-ceramic emission spectra of the samples with composition G2 thermal treated at different temperatures and times. As can be seen, more crystalline sample possesses more intensive emission spectrum. Moreover, the peaks are more split presenting the more complicated structure of the crystallizing phase. In the Ca₅Ge₃O₁₁ compound structure, calcium ions occupy five different crystallographic positions, so the peak split is not unexpected.

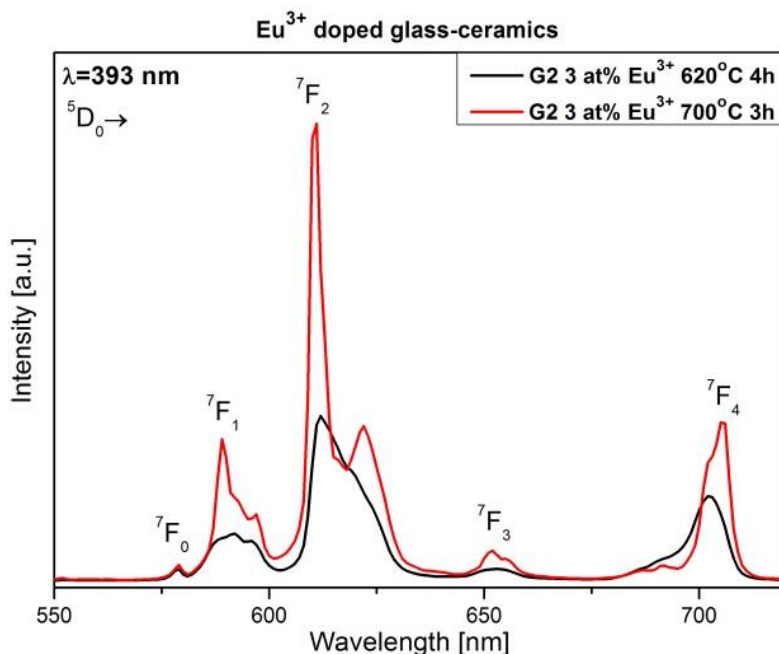


Fig. 5. Eu^{3+} doped glass-ceramic emission spectra of the samples with composition G2 thermal treated in different regimes.

Dy^{3+} doped glass-ceramic excitation and emission spectra are presented in Figure 6.

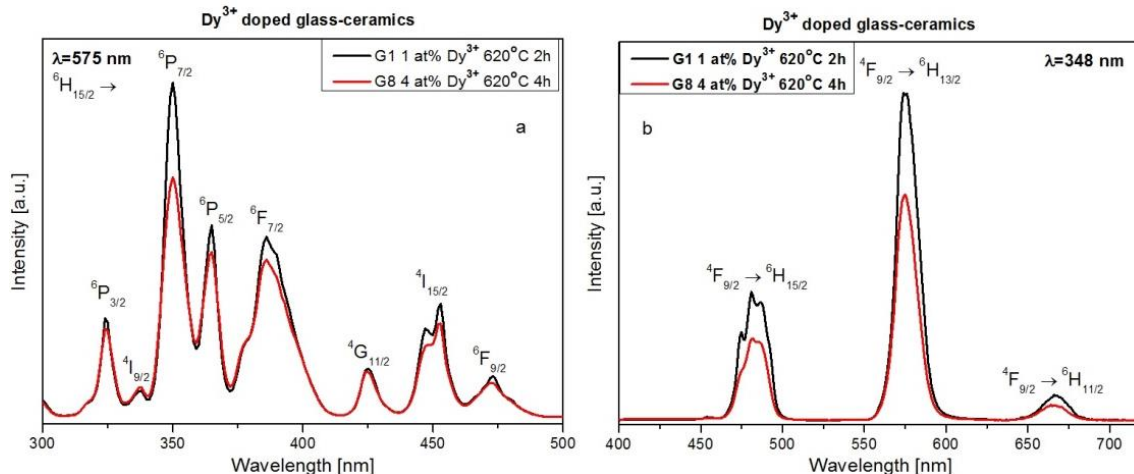


Fig. 6. Dy^{3+} doped glass-ceramic a) excitation and b) emission spectra

The excitation spectra of Dy^{3+} doped glass-ceramics in the range 300-500 nm, monitored at 575 nm, contains sharp lines assigned to the transitions: ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{3/2}$ (324 nm), ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{9/2}$ (337 nm), ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{7/2}$ (350 nm), ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{5/2}$ (365 nm), ${}^6\text{H}_{15/2} \rightarrow {}^6\text{F}_{7/2}$ (388 nm), ${}^6\text{H}_{15/2} \rightarrow {}^4\text{G}_{11/2}$ (424 nm), ${}^6\text{H}_{15/2} \rightarrow {}^4\text{I}_{15/2}$ (453 nm) and ${}^6\text{H}_{15/2} \rightarrow {}^4\text{F}_{9/2}$ (472 nm). These transitions are already published in the literature [13, 31]. The most intensive peaks occur at 348 nm. The emission spectra are monitored at 348 nm excitation in the range 400-720 nm. Dysprosium ion possesses three emission bands: a magnetic dipole transition (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) in the blue region, slightly depending on the surrounding; a hypersensitive electric dipole transition (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) in the yellow region and a weak transition in the red region (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$). Sharpe peaks are observed, because of the Stark levels splitting [32].

Peak areas in the luminescence spectra and Yellow-to-Blue (Y/B) ratio are presented in Table 3. As it is seen, the dominant peak in both glass-ceramics emission spectra is the yellow one. The Y/B ratio is closed; therefore the near emitted colors are expected.

Glass-ceramic	Blue area	Yellow area	Y/B
G1	$2.912 \cdot 10^8$	$6.622 \cdot 10^8$	2.274
G2	$1.868 \cdot 10^8$	$4.567 \cdot 10^8$	2.445

Table 3. Peak areas and Yellow-to-Blue (Y/B) ratio in the luminescence spectra of Dy^{3+} doped glass-ceramics

CIE coordinates of the glass-ceramics are presented in Table 4 and Figure 7.

Active ion	Tb^{3+}		Eu^{3+}		Dy^{3+}	
	x	y	x	y	x	y
G1	0.339	0.574	0.648	0.350	0.412	0.436
G2	0.365	0.559	0.652	0.347	0.412	0.440

Table 4. CIE coordinates of glass-ceramics doped by Tb^{3+} , Eu^{3+} , and Dy^{3+} ions.

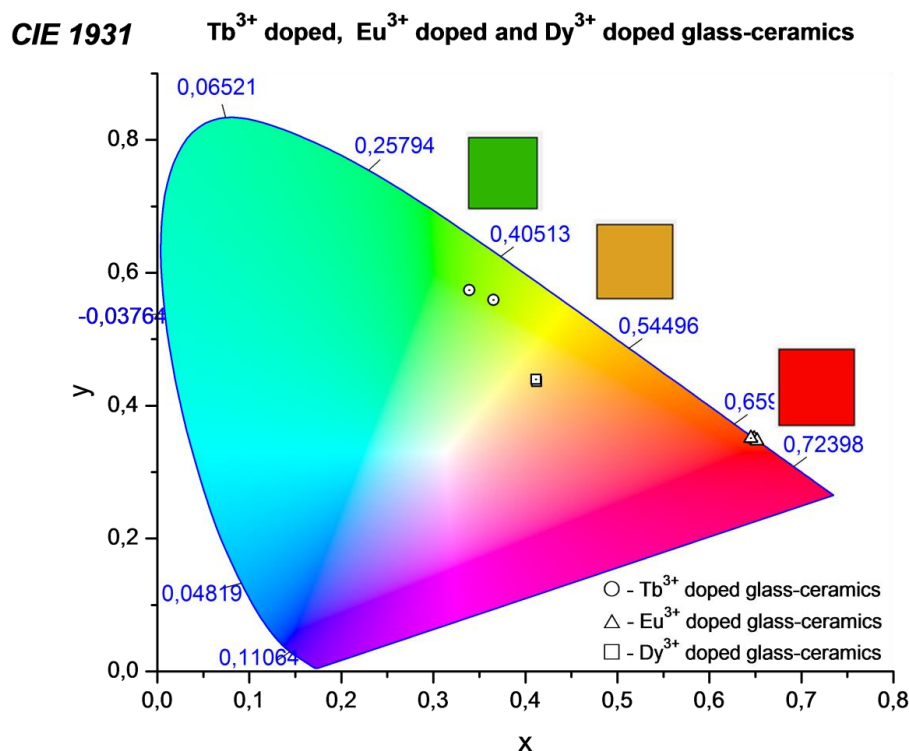


Fig. 7. CIE coordinates of glass-ceramics doped by Tb^{3+} , Eu^{3+} and Dy^{3+} ions.

Chromaticity coordinates of Tb^{3+} doped samples are placed in a green and green-yellowish part of the diagram. Chromaticity coordinates of Eu^{3+} doped samples are almost the same place in the red part of

the diagram. Chromaticity coordinates of Dy^{3+} doped samples are placed in a narrow area in the yellow part of the chromaticity diagram.

4. CONCLUSIONS

Glasses with two different compositions doped by Tb^{3+} , Eu^{3+} , or Dy^{3+} ions were prepared from the oxide system $\text{CaO-GeO}_2\text{-Li}_2\text{O-B}_2\text{O}_3$. After thermal treatment Ca_2GeO_4 or $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ crystallizes as the main phase. Unknown phase and Li_2GeO_4 as additional phases crystallize also. Thermal treatment conditions were determined from the DTA curves of the initial glasses. Excitation and emission spectra of the doped glass-ceramics contain the characteristic transitions of Eu^{3+} , Tb^{3+} , and Dy^{3+} ions. Some differences appear depending on the crystallizing phases. Glass-ceramic luminescence spectra where $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ crystallizes as the main phase are more split, as there are more possible crystallographic positions for the active ion. CIE coordinates of Eu^{3+} doped samples are placed in a very narrow area in the red part of the chromaticity diagram. CIE coordinates of the Tb^{3+} ion are more widely located in the green region. CIE coordinates of the Dy^{3+} ion are in a narrow area in the yellow chromaticity part. The studied glass-ceramics could be used as red, green, and yellow phosphors. It can be concluded that the obtained glass-ceramics could be suitable for LED applications.

ACKNOWLEDGMENTS

The research is financial supported by the National Science Fund of Bulgaria (Contract No. KP-06-H29/10). Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science was used in this investigation.

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