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$Ca_2GeO_4:Cr^{4+}$ transparent nano-glass ceramics

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ABSTRACT

The purpose of this study was to find out glass compositions permitting to obtain glass-ceramics of the Cr^{4+}:-Ca_2GeO_4 nanophase with a proper condition of syntheses and satisfying the requirements for transparent glass-ceramic. Three series of glass compositions were investigated, containing CaO, GeO_2 and the glass formers: $CaO\text{-}GeO_2\text{-}B_2O_3$, $CaO\text{-}GeO_2\text{-}Na_2B_4O_7$ and $CaO\text{-}GeO_2\text{-}LiBO_2$. The comparison between the three systems clearly shows that $CaO\text{-}GeO_2\text{-}LiBO_2$ offers significantly better conditions for obtaining glass ceramics containing Ca_2GeO_4 nanophase, as regards the temperature of melting and homogenization of the glasses (1100–1150 °C) and the possibility of obtaining Ca_2GeO_4, as a phase into the glass. It was established that because of the big difference between the speed of nuclei and the speed of particle growth, particles at about 50 nm at high degree of crystallization can be received. Transmission and photoluminescence spectra are measured and show that the active ion is Cr^{4+}. A broad–band of emission in the range of 1000–1600 nm was established.

1. Introduction

Tunable and femtosecond lasers emitting in the near 1.1–1.6 μm IR region find growing application in spectroscopy, ecology, medicine, etc. [1–3]. The most often used laser active media for these lasers are the chromium-doped forsterite ($Cr:Mg_2SiO_4$) and the chromium-doped garnet (Cr:YAG) [4,5]. The preparation of high-quality single crystals from these compounds is, however, bound to difficulties, mostly related to their high melting temperatures (1900 °C for forsterite and 1950 °C for garnet). These compounds also have drawbacks as laser media along with the targeted Cr^{4+}, a large part of the chromium dopant is in the form of Cr^{3+}. The Cr^{3+}/Cr^{4+} ratio strongly depends on the conditions of crystal synthesis [6,7]. Owing to non-radiation transitions, the efficiency of Cr^{4+} radiation is low. This efficiency drops on elevating the temperature, reaching only about 10% for forsterite and about 20% for garnet at room temperature [8–10]. All this fosters the search of new laser media.

$Cr:Ca_2GeO_4$ is another perspective laser medium. Ca_2GeO_4 has olivine structure, it is an analogue of Mg_2SiO_4, but differently from the latter, where part of magnesium can be substituted by Cr^{3+}, the substitution of Cr^{3+} for calcium is hardly likely due to the different valent states and sizes of the Ca^{2+} and the Cr^{3+} ions. Of significance is also the closeness of the ionic radii of Cr^{4+} and Ge^{4+} (0.41 Å and 0.39 Å, respectively), which presupposes an easy substitution of chromium for germanium up to high chromium concentrations [11]. Studies have shown that Cr^{4+} in Ca_2GeO_4 has a longer life in excited state and consequently, a higher efficiency. Unfortunately, the preparation of Ca_2GeO_4 single crystals is a hard task. Ca_2GeO_4 undergoes polymorphous transition at 1450 °C and single crystals with olivine structure can only be obtained below this temperature. In other words, Ca_2GeO_4 crystals can only be obtained from high-temperature solutions (by the flux method). For the growth of Ca_2GeO_4 crystals by this method, $CaCl_2$, $CaCl_2\text{-}CaF_2$ and CaF_2 have been tested as solvents. The use of $CaCl_2$ is accompanied by its evaporation [12], while the use of CaF_2 requires temperatures above 1350 °C, leading to evaporation of both CaF_2 and GeO_2.

A known alternative of single crystals for various applications are the transparent glass-ceramics with a nanosized phase crystallizing in the bulk of the glass. Some examples for chromium-doped glass-ceramics are already published [13–16]. Cr^{4+} doped glass-ceramics with Ca_2GeO_4 nanoparticles are obtained too [17,18].

There are a number of requirements to glass-ceramics for various applications, as follows [19,20]:

- The composition of the initial glass should provide relatively low temperature of melting and homogenization in order to avoid evaporation of its constituents;
- The initial glass should possess suitable viscosity and thermal properties in order to permit its cooling without breakage or partial crystallization;
- During devitrification, the glass composition should provide crystallization of the target phase only, with high concentration for high emission efficiency and phase size within 20–100 nm for preserving glass transparency.

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The obtained so far Cr^{4+}:Ca_2GeO_4 glass-ceramic possess the following disadvantages [17]:

- The temperatures of melting and homogenization are in the range of 1400–1500 °C, at which GeO_2 and Cr_2O_3 partially evaporate;
- Along with the target Ca_2GeO_4 phase, several other phases crystallize ($LiBGeO_4$ and an unknown phase);
- The particles have a mean size of about 1 μm, which is far from the desired nanosize.

The purpose of this study was to find out other glass compositions permitting to obtain glass-ceramics of the Cr^{4+}:Ca_2GeO_4 phase with properties satisfying to a high degree the requirements mentioned above.

2. Experiment

Three series of glass compositions were used, containing CaO, GeO_2 and the glass formers: CaO-GeO_2-B_2O_3, CaO-GeO_2-$Na_2B_4O_7$ and CaO-GeO_2-$LiBO_2$ compositions. Each of the series consisted of glasses with different weight ratios of the components. Boric oxide was included in all three series in order to lower the temperature of melting and homogenization and to increase viscosity (suppression of crystallization during glass cooling). The reagents used were $CaCO_3$ (99.9%), Li_2CO_3 (99.98%), Na_2CO_3 (99.98%), H_3BO_3 (99.8%) and GeO_2 (99.999%). To each composition 1 wt% of Cr_2O_3 with respect to the GeO_2 was added. The starting reagents taken at the necessary ratio in an overall amount of 5 g were primarily mixed and after that melted and homogenized in a platinum crucible. The process was performed in a chamber furnace with $MoSi_2$ heaters (up to 1700 °C) with temperature control within ±1 °C. The term "temperature of melting and homogenization" (T_{glass}), which will be used in further discussions, refers to the minimal temperature at which a homogeneous transparent glass mass is obtained within 6 h. Glasses with T_{glass} exceeding 1500 °C were not further considered because of evaporation of the B_2O_3 and GeO_2. The glass mass was poured between two steel plates and let to cool to room temperature. The obtained glasses were annealed at 400 °C for 24 h by gradually increasing the temperature to this value for 10 h maintain the last temperature for a 4 h and subsequent cooling for 10 h. The annealed glasses were devitrificated at various temperatures and holding times aiming that the glass remained transparent, but with partial crystallization.

Table 1
Initial glass compositions in the system CaO-GeO_2-B_2O_3, temperature of melting and homogenization (T_{glass}) and crystallizing phases after devitrification at 700–900 °C for 2 to 6 h.

No	Initial glass composition CaO-GeO_2-B_2O_3 [wt%]	T_{glass} [°C]	Crystallizing phases
1	45–45–10	1180	$CaGeO_3$ + $Ca_5Ge_3O_{11}$
2	40–40–20	1150	$CaGeO_3$ + $Ca_2B_2O_5$
3	35–35–30	1100	Unknown + CaB_2O_4
4	30–30–40	1060	CaB_2O_4
5	25–25–50	1020	CaB_2O_4
6	50–35–15	1250	$CaGeO_3$ + $Ca_2B_2O_5$ + CaB_2O_4
7	50–20–30	1150	$CaGeO_3$ + $Ca_2B_2O_5$ + CaB_2O_4
8	65–27–8	>1500	$Ca_3B_2O_6$ + Ca_2GeO_4
9	60–25–15	1500	Ca_2GeO_4 + $Ca_3B_2O_6$ + Ca_3GeO_5
10	57–40–3	>1500	$Ca_3B_2O_6$ + Ca_2GeO_4
11	55–35–10	1350	$Ca_5Ge_3O_{11}$
12	60–37–3	>1500	$Ca_3B_2O_6$ + Ca_2GeO_4
13	58–32–10	1400	$Ca_3B_2O_6$ + Ca_2GeO_4
14	45–40–15	1160	$Ca_2B_2O_5$ + unknown

The composition of the crystallized phase was determined by X-ray analysis. Powder XRD data were recorded in the range from 20 to 50° (2θ) with a constant step of 0.02° and 1 s/step counting time at room temperature on a Shimadzu XRD-7000 powder diffractometer using filtered Cu Kα radiation. The crystallite size and the degree of crystallinity were determined for glass where Ca_2GeO_4 crystallized only. Crystallite size was calculated by Bruker Diffrac EVA software using the FWHM of (113), (121) peaks and Scherrer equation. Degree of crystallinity was roughly calculated by the ratio between the area of crystalline peaks and the total area below the diffraction curve by Bruker Diffrac TOPAS software.

The TEM micrographs of powdered glass-ceramic samples were obtained using TEM JEOL JEM 2100 equipment at accelerating voltage 200 kV and 50,000 magnification.

The transmission spectra of some glass-ceramic after devitrification were tested on polished specimen plates with 1 mm depth. Spectra in the region 185–1800 nm were tested using Cary 6000i UV–VIS-NIR spectrophotometer (Varian).

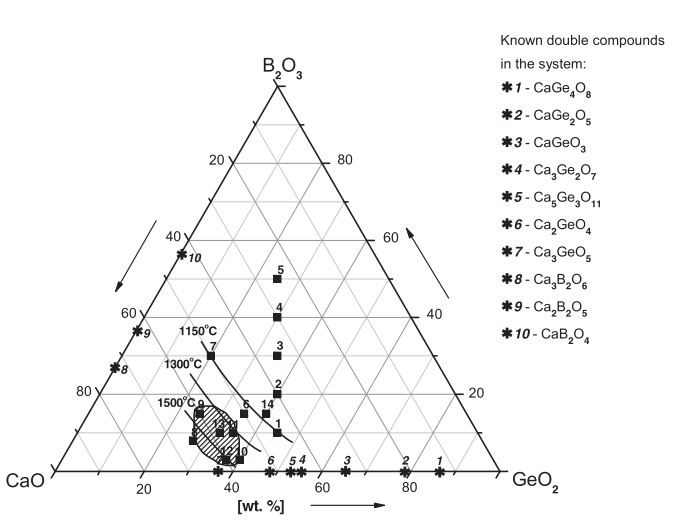

Fig. 1. System CaO-GeO_2-B_2O_3:-■-13 – initial glass compositions; ◌ – region of the glass compositions in which Ca_2GeO_4 nanophase crystallizes.

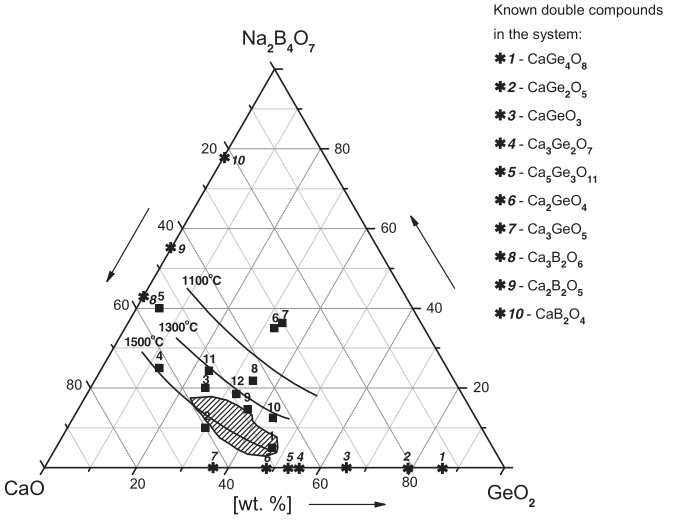

Fig. 2. System CaO-GeO_2-$Na_2B_4O_7$:-■-12 – initial glass compositions; ◌ – region of the glass compositions in which Ca_2GeO_4 nanophase crystallizes.

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