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Space-selective enhancement of blue photoluminescence in gallium germanosilicate glass through laser-induced nanostructuring

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ABSTRACT

Crystalline gallium oxide is known to possess UV-excited blue photoluminescence together with one of the widest band gaps among transparent conducting oxides, with a transmittance range extending from the visible to the near-UV range, thus making it a promising material for efficient solar-blind UV-to-visible converters. In the present paper, we report for the first time laser-induced space-selective precipitation of γ-Ga_2O_3 nanosized crystals in alkali gallium germanosilicate glass using a sum frequency beam (271 nm) of a copper vapor laser. At the glass surface, the laser writing process generates transparent nanostructured channels which emit broadband blue photoluminescence (centered at about 460 nm) under UV exposure, with excitation efficiency peaked at about 260 nm. Only much weaker blue photoluminescence can instead be observed in the starting non-irradiated glass from the precursor stage of the nanocrystallization. Spectral properties of light emission in the nanocrystallized regions are similar to those of earlier studied bulk nanostructured material produced from the same composition by heat treatment. Laser-written photoluminescent patterns in the studied glass provide advanced opportunities for developing novel solar-blind UV detectors.

1. Introduction

Gallium oxide nanostructures draw increasing attention since Ga_2O_3 is known as transparent semiconductor with one of the widest band gaps, promising for applications in the fields of light-emitting materials, optoelectronics, communications and sensors. One of their practically important properties—occurring both in stable β-Ga_2O_3 and metastable γ-Ga_2O_3 phases—is the intense light emission in the blue or green spectral region, UV-excited below 280 nm, observed in free nanocrystals [1], nanorods and nanowires [2,3] or their colloidal suspensions [4]. Together with the absence of optical absorption and excitation channels in the visible and near-UV ranges, the UV-excited light emission properties make Ga-oxide nanostructures promising material for the development of fully inorganic solar-blind UV-to-visible converters and UV viewers. However, in terms of device feasibility, bulk materials would be far more favorable than colloidal systems or nanopowders.

Precipitation of β-Ga_2O_3 nanocrystals was demonstrated in K_2O–Ga_2O_3–SiO_2 glasses [5]. Furthermore, NiO-doped alkali gallium silicate [6,7] and germanosilicate [8–10] glasses were shown to be efficient media for heat-treatment-induced precipitation of spinel-like γ-Ga_2O_3 or $LiGa_5O_8$ nanocrystals with almost total migration of Ni^{2+} ions into the nanophase, giving rise to broadband IR luminescence activity. Importantly, nanocrystallization practically does not impair transparency and optical homogeneity of these glasses. Moreover, alkali gallium silicate and germanosilicate glasses enable Ga-oxide nanocrystallization even without NiO doping. In such systems, we have recently collected evidence of broadband blue luminescence similar to that of Ga_2O_3 nanopowders, opening up opportunities for the development of novel light-emitting devices [11].

Over the last two decades, different laser-induced space-selective glass modification techniques have been developed and have enabled, in particular, the fabrication of 2- and 3-dimensional

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crystalline architectures in glass, promising for applications in integrated optics (reviewed in [12–14]). Still, most of studies on laser-induced glass crystallization concerned fabrication of nonlinear optical quasi-single-crystalline patterns in glasses, whereas only in the last few years some researchers also reported space-selective initiation or modification of light-emitting properties mainly obtained through laser-induced nanocrystallization [15–17]. Recently, our group has proposed a technique of laser-induced patterning in NiO-doped alkali gallium germanosilicate glass [18] including space-selective formation of γ-Ga_2O_3 nanocrystals. As a result of such process, broadband near-IR photoluminescence has been obtained, accompanied by significant increase of refractive index in the laser-treated regions, thus providing the opportunity for fabrication of active channel waveguides for applications in integrated optics.

In this work, we have studied the feasibility of space-selective generation of UV-excited blue luminescence activity using a laser-assisted technique for the fabrication of light-emitting nanostructures in alkali gallium germanosilicate glass.

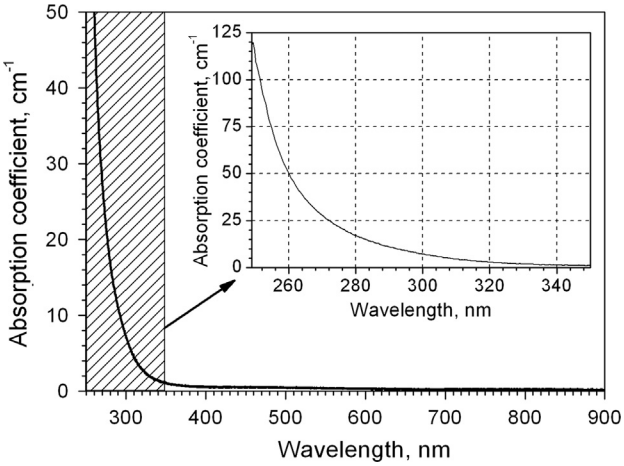

Fig. 1. Absorption spectrum of the starting glass. An inset shows a more detailed spectrum in the UV range.

2. Experimental

$7.5Li_2O \cdot 2.5Na_2O \cdot 20Ga_2O_3 \cdot 45GeO_2 \cdot 25SiO_2$ glass was synthesized from reagent-grade SiO_2, GeO_2, Ga_2O_3, Li_2CO_3 and Na_2CO_3. Samples were obtained by a conventional melt quenching technique by analogy with [8]. Melting was performed in a platinum crucible at 1480 °C for 80 min. To improve homogeneity and to provide oxidizing conditions, the melt was bubbled with oxygen for 60 min. Then the melt was quenched by pouring into a steel mold at room temperature. The as-quenched glass was cut and polished into 1 mm thick plates. Absorption spectrum of the glass was obtained using a Cintra 303 UV-visible spectrophotometer. A Netzsch STA404 F3 Jupiter thermal analyzer was used for differential scanning calorimetry. Kulon-10 Cu–M industrial copper vapor laser (CVL) was employed in the material irradiation process. Since the studied glass does not absorb fundamental lines of the CVL (510.6 and 578.2 nm), we used Kulon-10 Cu–M–UV version equipped with a nonlinear frequency converter based on BBO crystal and producing a sum frequency of fundamental lines in the UV range (271 nm, pulse duration 10 ns, repetition rate up to 12.8 kHz, average power ~0.25 W) [19]. The beam was focused on the surface of the sample through a lens with 47 mm focal length. Samples were irradiated inside a furnace with a UV-transparent silica glass cover and the temperature was controlled using a thermocouple near the sample surface. The furnace was mounted on an XY-axes motorized stage providing horizontal translation with a variable speed 25–200 μm/s. A layout of the setup can be found in [20]. Microscopy analysis of the samples was performed using an Olympus BX51 microscope. Photoluminescence spectra were recorded with a spectrofluorimeter based on MS3405i monochromator (SOL instruments Ltd.) using a high-pressure xenon lamp for excitation. X-ray diffraction (XRD) of powdered and bulk samples was performed using a Bruker D2 Phaser diffractometer.

3. Results and discussion

The fabricated glass was visually colorless and transparent. Its absorption spectrum (Fig. 1) confirms the absence of absorption in the visible range. In the UV region, the absorption coefficient increases to about 26 cm^{-1} at 271 nm providing efficient absorption of the sum-frequency line of the CVL.

DSC curve of the studied glass (not shown here) is similar to that reported earlier for a similar composition [8] with characteristic temperatures only slightly different, being 560 °C for glass transition (T_g), 655 °C and 670 °C for onset and maximum of the exothermic crystallization peak, respectively. Heat-assisted irradiation of the samples by the focused laser beam moving along the glass surface results in formation of visible transparent lines in the irradiated areas. To avoid cracking of the sample caused by thermal stress and to facilitate crystallization, irradiation was performed at 530–540 °C, just below T_g. Actually, a slow temperature variation of the whole sample may occur during irradiation because of heat dissipation from the irradiated area.

Visual detection of photoluminescence was performed under UV light with the sample out of the focus of a beam of a xenon lamp emission selected by a monochromator at 254 nm (Fig. 2). The depth of the luminescent region was evaluated by microscopy analysis of the cross-section (Fig. 2(j)) for a line obtained at maximal laser power and 100 μm/s scan speed (Fig. 2(c)).

Excitation and emission spectra for the laser-treated glass are shown in Fig. 3 together with an emission spectrum for the non-treated as-quenched glass. Excitation spectrum of the sample was corrected for the nominal emission spectrum of the exciting lamp. Spectra are normalized with respect to the maximum of the emission band in the irradiated area. Spectra of irradiated material were recorded from a wide laser-treated area obtained by consecutive laser scanning (Fig. 3, inset) so that the excitation spot was fully within this luminescent area. The broad luminescence band centered at around 460 nm (Fig. 3, curve *a*) resembles the light emission expected from radiative recombination at donor and acceptor pairs in β-Ga_2O_3 and γ-Ga_2O_3 [1–4]. The onset of luminescence excitation at about 260 nm (Fig. 3, curve *b*) matches the excitation features related to the direct allowed optical gap of Ga_2O_3 crystalline phases, and confirms the blue luminescence band as an indicator of Ga_2O_3 crystallization in the laser-treated regions.

An XRD pattern for the irradiated sample was obtained for the same bulk sample with the large luminescent area whereas a powder XRD pattern was obtained for the as-quenched glass (Fig. 4). Evaluation of nanocrystal size by using Scherrer's equation to [311] and [440] peaks gives values in the range 4–12 nm, similarly to bulk nanocrystallized glasses (6–8 nm) [9,10]. Both XRD and spectral data suggest the occurrence of an initial phase separation during glass quenching, with very broad structures overlapped to the amorphous XRD halo and much weaker photoluminescence. Laser treatment strongly enhances photoluminescence, giving rise to the growth of γ-Ga_2O_3 nanocrystals, as confirmed by the XRD pattern of the laser-treated glass (Fig. 4, line b), showing