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Photoluminescence of transparent glass-ceramics based on ZnO nanocrystals and co-doped with Eu^{3+}, Yb^{3+} ions

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ABSTRACT

Glasses of the K_2O–ZnO–Al_2O_3–SiO_2 system co-doped with Eu_2O_3 and Yb_2O_3 were prepared by the melt-quenching technique. Transparent zincite (ZnO) glass–ceramics were obtained by secondary heat-treatments at 680–860 °C. At 860 °C, traces of Eu oxyapatite appeared in addition to ZnO nanocrystals. The average crystal size obtained from the X-ray diffraction data was found to range between 14 and 35 nm. Absorption spectra of the initial glasses are composed of an absorption edge and absorption bands due to electronic transitions of Eu^{3+} ions. With heat-treatment, the absorption edge pronouncedly shifts to the visible spectral range. The luminescence properties of the glass and glass-ceramics were studied by measuring their excitation and emission spectra at 300, 78, and 4.2 K. Strong red emission of Eu^{3+} ions dominated by the $^5D_0$–$^7F_2$ (612 nm) electric dipole transition was detected. Changes in the luminescence properties of the Eu^{3+}-related excitation and emission bands were observed after heat-treatments at 680 °C and 860 °C. The ZnO nanocrystals showed both broad luminescence (400–850 nm) and free-exciton emission near 3.3 eV at room temperature. The upconversion luminescence spectrum of the initial glass was obtained under excitation of the 976 nm laser source.

1. Introduction

ZnO is an intensively studied wide band gap semiconductor (Eg = 3.37 eV) with various applications especially, in optoelectronics [1–10]. ZnO has been reported as a promising host for rare-earth (RE) ions [11–15]. It efficiently sensibilizes RE ions due to the energy transfer from ZnO to RE ions [16,17], which allows to overcome the low absorptions of parity-forbidden f–f transitions of RE ions. In recent years, there has been increasing interest in the development of RE ions doped ZnO quantum dots. RE ions doped glass-ceramics (GC) containing ZnO nanosized crystals are alternative materials to RE ions doped ZnO quantum dots as oppositely to quantum dots, ZnO nanocrystals are homogeneously distributed within the glass matrix without agglomeration. The materials are produced by a convenient melt-quenching technique, the properties are highly reproducible and are not deteriorated during storage. However, after the pioneer paper of L. Pinckney [18], there have been only few papers on spectral properties of GC containing volume crystallized ZnO nanocrystals including those doped with ions of transition and rare-earth (RE) elements [19–25], despite these materials show promise for the development of laser technology and optoelectronics [23–25]. It should be mentioned that there are some papers devoted to GC produced by surface crystallization of glasses [26–29] and GC produced via sol-gel route [30]. Partially crystallized samples containing ZnO crystals were obtained from supercooled melts [31]. ZnO nanocrystals were formed on the glass surface by laser pattering [32], space-selective precipitation of ZnO crystals in glass by using high repetition rate femtosecond laser irradiation was reported [33].

To the best of our knowledge, in this work for the first time initial glasses of the potassium-zinc-aluminum-silicate system co-doped with Eu^{3+} and Yb^{3+} were synthesized, transparent GC

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containing volume precipitated ZnO nanocrystals were prepared by secondary heat-treatments of these glasses and their structure and spectral luminescent characteristics were studied.

2. Experimental

2.1. Synthesis

A glass with the composition (mol%) $14K_2O$–$32ZnO$–$14Al_2O_3$–$40SiO_2$ was co-doped with 1 mol% Eu_2O_3 and 1 or 1.5 mol% Yb_2O_3 added above 100% of the base components. The raw materials for the glass preparation included reagent grade K_2CO_3, ZnO, Al_2O_3, and SiO_2. The raw materials were carefully mixed, and glasses of 400 g in weight were melted in crucibles made of quartz ceramics in a laboratory electric furnace at 1590 °C for 6 h with stirring, cast onto a cold metal plate and annealed at 500 °C in an annealing furnace. The differential thermal analysis (DTA) curve was performed with a home-made DTA instrument using the glass powder and corundum powder reference sample, the temperature range was from the room temperature to 1050 °C, the heating rate was 10 °C per minute.

X-ray diffraction (XRD) patterns of the powdered initial glasses and GC were measured using a Shimadzu XRD-6000 diffractometer, Cu K_α radiation with a Ni filter. The mean sizes of the crystals were estimated from the broadening of the X-ray peaks according to Scherrer's equation

$$D = K\lambda/(2\theta)\cos\theta, \quad (1)$$

where λ is the X-ray radiation wavelength, θ is the diffraction angle, $\Delta(2\theta)$ is the full width of the peak at half-maximum, and K is the Scherrer constant assumed to be 1 [34]. The error in the mean crystal size estimation is about 5%.

For the spectroscopic studies, including upconversion (UC) emission, 3-mm-thick polished plates of the initial glass co-doped with 1 mol% Eu_2O_3 and 1.5 mol% Yb_2O_3 and of the GC co-doped with 1 mol% Eu_2O_3 and 1 mol% Yb_2O_3 were selected. Optical absorption spectra were measured in the spectral range from 0.25 to 0.9 μm with a Shimadzu UV 3600 spectrophotometer.

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded in the spectral range from 0.25 to 0.90 μm using an MDR–23U single-beam grating monochromator with the focal length of ~0.6 m and a diffraction grating with 1200 grooves per mm (reciprocal linear dispersion 13 Å/mm). All spectra were measured using a DKSEL–1000 xenon lamp with a power of 1000 W as a light source. The xenon lamp light was dispersed by an MDR–12 monochromator with a focal length of ~0.3 m and a diffraction grating with 1200 grooves per mm (reciprocal linear dispersion 26 Å/mm). This monochromator was used to record luminescence excitation spectra. PL spectra were also excited at 325 nm by a He–Cd gas laser with a power up to 25 mW. The spectrum was detected using a Hamamatsu R9110 photomultiplier. The light of the lamp or the laser light source was modulated by a mechanical modulator at a frequency of ~20 Hz. The spectra were recorded by the synchronous phase detection using a two-channel synchronous detector, from which the digital code was transferred to the computer for automatic spectrum recording. The PL spectra were measured at room temperature and at the temperatures of liquid nitrogen, 78 K, and liquid helium, 4.2 K, with the samples immersed in the liquid cooling agent in special cryostats. The PL spectra and the PLE spectra were adjusted to the spectral characteristic of the detection system and to the spectral density distribution of the exciting beam.

The room temperature UC emission spectrum of the Eu^{3+}/Yb^{3+} co-doped initial glass was optimized for maximum PL intensity under the 976 nm excitation of a mode-locked picosecond laser (EKSPLA, PT257-SOPO). The laser beam was focused into the sample by a 40× objective lens. The UCL spectrum was analyzed with the monochromator-spectrograph MS-5004i coupled with a CCD camera. The addition of Yb^{3+} ions promotes the UC emission of Eu^{3+} ions as Yb^{3+} plays a role of a sensitizer due to its strong absorption cross section in the NIR range with a maximum at 976 nm [35].

3. Results and discussion

Initial glasses were transparent and yellow colored, the glass co-doped with 1 mol% Eu_2O_3 and 1.5 mol% Yb_2O_3 was slightly opalescent. According to the DTA study, for the glass co-doped with 1 mol% Eu_2O_3 and 1.0 mol% Yb_2O_3 the glass transition temperature, T_g, was 690 °C; ZnO was the first phase that crystallized as temperature increased. Based on these results, the temperatures of secondary heat-treatments ranged from 680 to 860 °C were selected; and the heat-treatment durations were 2–12 h. For the detailed study, the glass containing 1 mol% Eu_2O_3 and 1.5 mol% Yb_2O_3 (the sample 1), and GC containing 1 mol% Eu_2O_3 and 1.0 mol % Yb_2O_3 (samples 2 and 3) prepared by heat-treatments at 680 °C for 12 h and at 860 °C for 2 h respectively were selected.

After heat-treatments at 680–800 °C, the samples remained transparent though acquired a bluish color; at elevated temperatures, opalescence increased with increasing heat-treatment temperature, the samples became translucent and then opaque.

3.1. XRD study

The XRD patterns of the initial and heat-treated glasses are shown in Fig. 2. Both initial glasses are X-ray amorphous. Zinc oxide nanocrystals with a size of ~14 nm appeared after the heat-treatment of the initial glass co-doped with 1 mol% Eu_2O_3 and 1 mol% Yb_2O_3 at 680 °C for 12 h. Thus obtained GC sample is transparent. The XRD pattern of the GC prepared by the heat-treatment at 860 °C for 2 h demonstrates crystallization of two phases, i.e., ZnO crystals with a size of ~35 nm and traces of oxyapatite crystals with the general formula $RE_{4.67}O_{0.33}[SiO_4]_3O$, where is a vacancy. The ZnO crystallinity fraction increases about 4 times with increasing heat-treatment temperature. The sample is translucent. The images of the samples under study are presented in Fig. 1.

3.2. Absorption spectroscopy

Absorption spectra of the initial glasses and the GC samples are shown in Fig. 3. The absorption spectra of the initial glasses are very similar; the difference is only in the position of the absorption edge, which is shifted to higher wavelengths for the sample with a higher Yb_2O_3 content due to light scattering caused by amorphous phase separation. In the visible spectral range, the absorption bands in the initial glasses are assigned to electronic transitions from the $^7F_0$

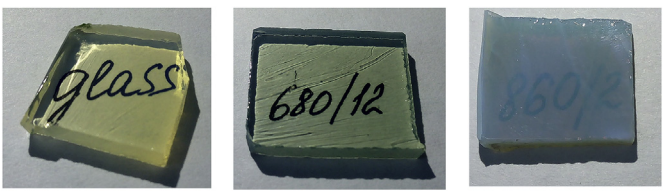

Fig. 1. The images of the samples under study. The figures stand for heat-treatment schedule (temperature, °C/duration, h).

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