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Structural characteristics and spectral properties of novel transparent lithium aluminosilicate glass-ceramics containing (Er,Yb)NbO_4 nanocrystals

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ABSTRACT

Transparent lithium aluminosilicate glass-ceramics based on nanosized crystals of β-quartz solid solutions and Er,Yb orthoniobates are prepared for the first time, to our knowledge. According to X-ray diffraction analysis, parent Er,Yb-codoped glass contains (Er,Yb)NbO_4 nanocrystals with the defected fluorite structure while the single Yb-doped glass is X-ray amorphous. The Er,Yb orthoniobates with the tetragonal structure crystallize under heat-treatments at 800–900 °C; and at 1000 °C the transformation to a monoclinic form begins. β-quartz solid solutions are the main crystalline phase of glass-ceramics prepared in the temperature range of 800–1000 °C. These structural transformations are confirmed by Raman spectroscopy. The structure evolution is illustrated by the TEM study of the Yb-doped glass and glass-ceramics. The spectral-luminescent properties of glass-ceramics are directly linked to their structure; an appearance of the monoclinic phase has a crucial effect on these properties. Glass-ceramics with tetragonal (Er,Yb)NbO_4 nanophase are characterized by the high efficiency of $Yb^{3+} \rightarrow Er^{3+}$ energy transfer (85%), strong absorption in the vicinity of 0.98 μm and shorter lifetime of $^4I_{13/2}$ state (as compared with the parent glass), so they look promising for laser operation in the eye-safe region around 1.53 μm.

1. Introduction

Among other Er-doped crystals [1–15], erbium orthoniobates are promising luminescent materials [16,17]. Until now, several routes for their preparation were employed. The growth of bulk monoclinic $ErNbO_4$ single crystals from the melt at ~1800 °C was reported in Ref. [18]. Monoclinic $ErNbO_4$ phase with size of 10–20 nm was detected in $LiNbO_3$ heavily doped with erbium oxide (around 2 mol%) by a vapor transport equilibration treatment [19,20]. These crystals were also found in sol–gel grown Er-doped lithium niobate ($LiNbO_3$) ceramics [21].

Zhang et al. conducted a series of studies of nanosized crystals of monoclinic $ErNbO_4$ [16,17,22,23] synthesized by direct powder calcination of Er_2O_3 and Nb_2O_5 compounds [22]. Raman spectroscopy [23], X-ray diffraction (XRD) studies [22], optical absorption and 1.54 μm luminescence [16,17,23] of these crystals were reported. In addition, intense green and red up-conversion luminescence was detected [16,17].

An appearance of the $YbNbO_4$ phase at 10% Yb^{3+} doping was demonstrated in $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped $NaNbO_3$ nanocrystals prepared by a sol–gel method [24]. The route for enhancement of up-conversion luminescence (UCL) by sensibilization of $ErNbO_4$ with ytterbium, Yb^{3+}, was also shown [25]. The Er,Yb-codoping (providing the efficient energy transfer (ET), $Yb^{3+} \rightarrow Er^{3+}$) is a well-known approach for the enhancement of the 1.54 μm emission due to the strong absorption of ytterbium ions around 1 μm [26,27], the spectral region covered with commercially available InGaAs laser diodes.

The promising route for obtaining the nanosized $ErNbO_4$ and (Er,Yb)NbO_4 crystals could be the formation of transparent glass-ceramics with rare-earth niobate nanophase. Its advantages would be a simple synthesis procedure based on a standard melting–quenching technique for initial glass and subsequent heat-treatment providing precipitation of Er,Yb-containing niobate nanocrystals. Thus, all-solid

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large-volume material could be obtained. At the moment, transparent glass-ceramics with $ErNbO_4$ or $(Er,Yb)NbO_4$ nanocrystals have not been synthesized yet. In the present paper, we report on the spectral-luminescent study of novel lithium aluminosilicate transparent glass-ceramics containing nanocrystals of $(Er,Yb)NbO_4$ and β-quartz solid solutions (ss). This is the first realization of $(Er,Yb)NbO_4$-containing transparent glass-ceramics, to the best of our knowledge. It is also worth noting that the chosen synthesis method allows us to make the correlation between the spectral-luminescent properties and observed fluorite-to-tetragonal-to-monoclinic phase transition for $(Er,Yb)NbO_4$ nanocrystals. Previously, glass-ceramics for optical applications in the lithium aluminosilicate system were mainly studied from the point of view of different crystal hosts: nanosized crystals of β-quartz solid solutions and spinels doped with transition metal ions, i.e. Co^{2+} or Ni^{2+} ions [28], as well as rare-earth titanates $(Er,Yb)_2Ti_2O_7$ [29]; and this system demonstrates high potential for enhancement of active ion emission by the appropriate heat-treatment.

2. Experimental

The glass with the composition of 18 Li_2O, 27 Al_2O_3 and 55 SiO_2 (mol%) [30] was chosen for the study. It was doped with 2–5 mol% RE_2O_3 (where RE is Y, Er, Yb) and 2–5 mol% Nb_2O_5.

Batches to produce 300 g of glass were melted in crucibles made of quartz ceramics in a laboratory electric furnace at 1560 °C for 4 h with stirring. After stirring, the glass melt was bubbled by oxygen for 0.5 h to remove the hydroxyl groups from the melt. The glass melts were poured onto a metal plate; the glasses were annealed at 620 °C and heat-treated in isothermal conditions in the temperature range from 640 to 1100 °C for 6 h. For the detailed spectroscopic investigations, two glasses were prepared, one codoped with erbium, ytterbium and niobium oxides (Er_2O_3—0.15 mol%, Yb_2O_3—3.07 mol% and Nb_2O_5—3.22 mol%) and the other only ytterbium and niobium oxides doped (Yb_2O_3—3 mol% and Nb_2O_5—3 mol%).

X-ray diffraction (XRD) patterns of powdered parent glass and glass-ceramic samples were measured using a Shimadzu XRD-6000 diffractometer, Cu Kα radiation with a Ni filter. The mean crystal sizes were estimated from broadening of X-ray peaks according to Scherrer's equation:

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

where λ is the wavelength of X-ray radiation, θ is the diffraction angle, $\Delta(2\theta)$ is the width of peak at half of its maximum, and K is the constant assumed to be 1 [31]. The error in the mean crystal size estimation is about 5%.

Rietveld refinement [32] was performed using the MAUD program [33]. The X-ray diffraction patterns were collected in a step-scanning mode with steps of $\Delta 2\theta = 0.02^\circ$ in the 2θ range 10–120° in the preset time mode (1 s). Pure cubic Y_2O_3 powder standard sample was used to correct the data for instrumental broadening.

The structure of the parent glass and glass-ceramics was studied with the Transmission electron microscopy (TEM). For TEM studies, finely powdered samples were dispersed in etanol. The microscope used was JEOL TEM-1011 (100 kV acceleration voltage, 0.4 nm point resolution).

For the spectroscopic studies, the parent glasses and glass-ceramics heat-treated at 800, 900 and 1000 °C were used. They were thin (2 mm) polished plates. Raman spectra were recorded in backscattering geometry by using an InVia (Renishaw, England) Micro-Raman spectrometer equipped with the cooled up to −70 °C multichannel detector. Ar^+ laser line of 514 nm was employed as an excitation source. Leica 50× (NA=0.75) objective was used for illuminating the sample; the scattered light was collected by the same objective. Notch filter was placed before the spectrograph entrance slit. A spatial resolution of 2 cm^{-1} was obtained. Acquisition time was 60 s.

Optical absorption spectra were measured in the spectral range of 0.35–3.00 μm with a Varian CARY-5000 spectrophotometer, the spectral bandwidth (SBW) was 0.1 nm. The near-IR Er^{3+} luminescence was excited by a focused radiation of 960 nm InGaAs laser diode. It was collected by a wide-aperture lens and reimaged to the input slit of the monochromator MDR-23 (SBW=0.5 nm). The spectrum was detected with a lock-in amplifier and InGaAs Hamamatsu G5851 photodetector, the noise was subtracted.

The upconversion luminescence (UCL) was excited by a focused radiation of ~960 nm CW InGaAs laser diode. The corresponding emission spectrum was measured with a monochromator, lock-in amplifier and a Hamamatsu C5460-01 photodetector. The output power of the laser diode was scaled to determine the UCL intensity vs excitation power plots.

The decay of 1 μm Yb^{3+} emission for both Yb,Er-codoped and single Yb-doped samples, as well as 1.54 μm Er^{3+} emission (excited at 960 nm by means of ns output from the optical parametric oscillator, OPO), was detected with a monochromator MDR-12, the G5851 photodetector and 500 MHz Textronix TDS-3052B digital oscilloscope. For the decay measurements in the visible range (Er^{3+} emission), OPO was tuned to 518, 540 or 650 nm, and fast Hamamatsu C5460 photodiode was used. For the measurement of Yb^{3+} lifetime, fine powdered samples immersed in glycerin were used (in order to exclude the impact of self-trapping).

3. Results

The parent glasses and glass-ceramics were transparent; the samples became slightly haze only after heat-treatment at 1000 °C. Their images are shown in Fig. 1.

3.1. XRD and TEM study

The XRD patterns of the parent glasses and glass-ceramics prepared at 800, 900 and 1000 °C are presented in Fig. 2 (for the Er,Yb-codoped samples) and in Fig. 3 (for the single Yb-doped ones).

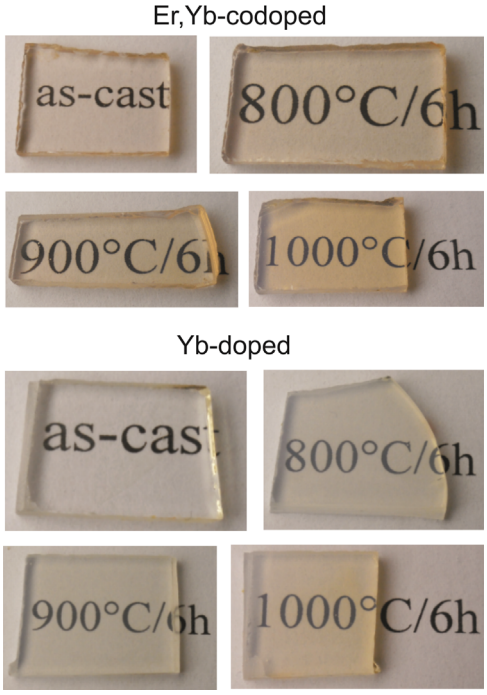

Fig. 1. Images of polished samples of Er,Yb-codoped and Yb-doped parent glasses and corresponding glass-ceramics prepared at 800, 900 and 1000 °C for 6 h. The values indicated in the figure denote heat-treatment temperatures.