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SPECTROSCOPIC AND LUMINESCENCE PROPERTIES OF ERBIUM IONS IN TRANSPARENT GLASS-CERAMICS CONTAINING (ER,YB)NBO_4 NANOCRYSTALS

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Abstract. Transparent glass-ceramics containing nanocrystals of (Er,Yb)NbO_4 and β-quartz solid solution have been prepared; their absorption spectra, IR and up-conversion luminescence spectra have been studied. Spectral-luminescent characteristics prove these materials to be promising media for 1.5 μm laser generation.

Materials doped with erbium and ytterbium ions attract attention as active media for 1.5 μm lasers. Radiation of such lasers lies within the atmosphere transparency region and is relatively eye-safe. Er-doped media based on phosphate glasses are most commonly used at present. However, their thermal conductivity is low. Crystals with Er^{3+} ions operating in the range of ~1.5 μm have long lifetimes of $^4I_{11/2}$ level. It results in negative processes of up-conversion and back energy transfer from Er^{3+} to Yb^{3+} ions.

New type of promising active media, transparent glass-ceramics doped with erbium and ytterbium ions was recently prepared. Relatively high thermal conductivity of glass-ceramics gives them an important advantage over glasses as active media. Low lifetime (4-5 μs) of $^4I_{11/2}$ level significantly reduces green up-conversion luminescence and increases the intensity of IR luminescence.

Glass-ceramics was obtained from the precursor lithium aluminosilicate glass doped by Er_2O_3, Yb_2O_3 and Nb_2O_5. Heat-treatment of the initial glass in the temperature range of 800 – 1000 °C leads to precipitation of (Er,Yb)NbO_4 nanocrystals in the glass matrix. The concentration of Er^{3+} and Yb^{3+} ions is 0.6×10^{20} cm^{-3} and 12×10^{20} cm^{-3} respectively. These crystals are the nucleators of volume crystallization of β-quartz solid solutions. X-ray diffraction (XRD) patterns of powdered samples were measured using Shimadzu XRD-6000 diffractometer, Cu K_α radiation with a Ni filter. Absorption spectra were measured by Cary Varian 5000 spectrophotometer. Luminescence has been excited by 962 nm cw laser diode. Luminescence spectra were registered by monochromator with lock-in amplifier.

According to XRD data (Fig. 1), rare-earth niobate nanocrystals with tetragonal structure precipitated in samples heat-treated at 800 -900 °C. Heat-treatment at 1000°C leads to precipitation of monoclinic (Er,Yb)NbO_4 nanocrystals.

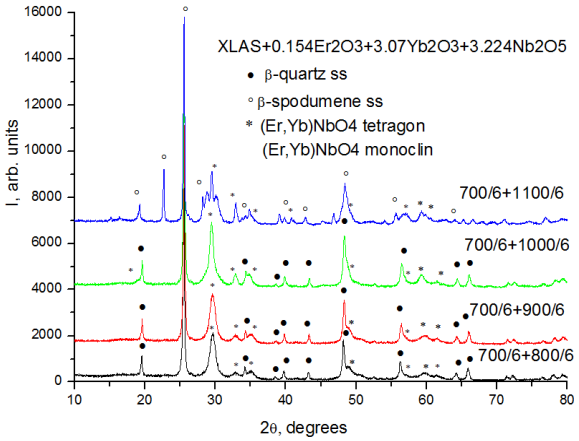

Fig. 1. X-ray diffraction of glass-ceramics

Figure 2 shows absorption spectra of erbium (a) and ytterbium (b) ions in initial glass and glass ceramics. Bands in the range 900–1000 nm are attributed to $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition of ytterbium ion and bands at 1450-1550 nm connected with $^4I_{15/2}\rightarrow{}^4I_{13/2}$ transition of erbium ion. Secondary heat-treatment at 800–900°C leads to absorption spectra structuring due to a change of the ligand field around erbium and ytterbium ions caused by the formation of (Er,Yb)NbO_4 nanocrystals (110-130 Å) with tetragonal structure.

Heat-treatment at 1000°C leads to a partial transformation of (Er,Yb)NbO_4 crystals into a monoclinic form, which resulted in additional Stark splitting of the absorption bands. Co- precipitation of nanosized (500 Å) crystals of β-quartz solid solutions (Fig. 1) does not change the shape of the absorption bands as large Er^{3+} and Yb^{3+} ions do not enter its structure. This crystalline phase ensures high thermal shock resistance of the prepared materials.

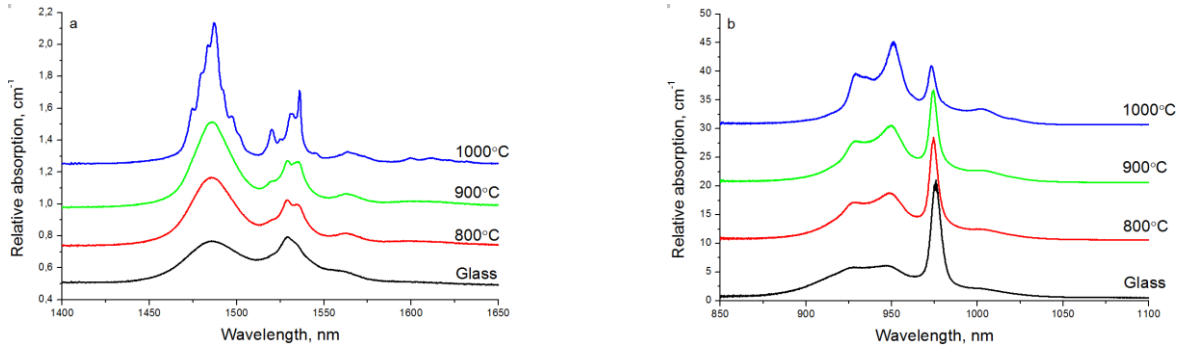

Fig. 2. Absorption spectra of Er^{3+} (a) and Yb^{3+} (b) ions in initial glass and glass-ceramics

Figure 3 presents up-conversion and near IR luminescence spectra of Er^{3+} ions in the initial glass and glass-ceramics. Luminescence bands in the green and red spectral ranges are attributed to transitions $^2H_{11/2}\rightarrow{}^4I_{15/2}$ (near 522 nm) and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ (near 545 nm) of Er^{3+} ions. The population of appropriate luminescence levels takes place due to excited state absorption and/or cross-relaxation processes while the $^4I_{11/2}$ level of Er^{3+} ions is populated predominantly due to energy transfer from the Yb^{3+} ion excited state $^2F_{5/2}$. Luminescence spectra near 1.5 μm correspond to $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} ions. Lifetime of Yb^{3+} ions in the $^2F_{5/2}$ state (~3 μs) and Er^{3+} lifetimes in the $^4I_{11/2}$ (~4-5 μs) and $^4I_{13/2}$ states (~0,9-1 ms) have been obtained.

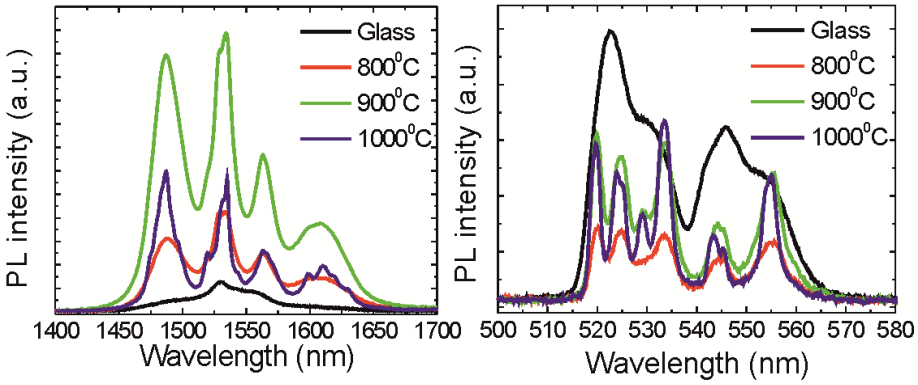

Fig. 3. IR and up-conversion luminescence spectra of Er^{3+} ions in the initial glass and glass-ceramics

After heat-treatment, luminescence spectra structuring and splitting is observed according to a change of the ligand field due to precipitation of tetragonal (Er,Yb)NbO_4 nanocrystals and their partial recrystallization into monoclinic (Er,Yb)NbO_4 nanocrystals. The decrease in the symmetry results in the increased splitting of the luminescence bands.

Conclusion

Transparent thermal shock resistant glass-ceramics composed of nanosized crystals of $ErYbNbO_4$ and β-quartz solid solutions has been prepared for the first time. It was shown that niobate nanocrystals doped with erbium and ytterbium ions have strong luminescence in the spectral region of 1.5 μm. Low lifetime of $^4I_{11/2}$ state for erbium ions reduces the intensity of up-conversion luminescence. Studied materials seem to be promising for 1.5 μm laser generation.