

SPECTROSCOPIC AND LUMINESCENCE PROPERTIES OF ERBIUM IONS IN TRANSPARENT GLASS-CERAMICS CONTAINING (ER,YB)NbO₄ NANOCRYSTALS

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Abstract. Transparent glass-ceramics containing nanocrystals of (Er,Yb)NbO₄ 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 μ m laser generation.

Materials doped with erbium and ytterbium ions attract attention as active media for 1.5 μ m 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 Er³⁺ ions operating in the range of \sim 1.5 μ m have long lifetimes of ⁴I_{1/2} level. It results in negative processes of up-conversion and back energy transfer from Er³⁺ to Yb³⁺ 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 μ s) of ⁴I_{1/2} 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 Er₂O₃, Yb₂O₃ and Nb₂O₅. Heat-treatment of the initial glass in the temperature range of 800 – 1000 °C leads to precipitation of (Er,Yb)NbO₄ nanocrystals in the glass matrix. The concentration of Er³⁺ and Yb³⁺ ions is 0.6 \times 10²⁰ cm⁻³ and 12 \times 10²⁰ 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)NbO₄ nanocrystals.

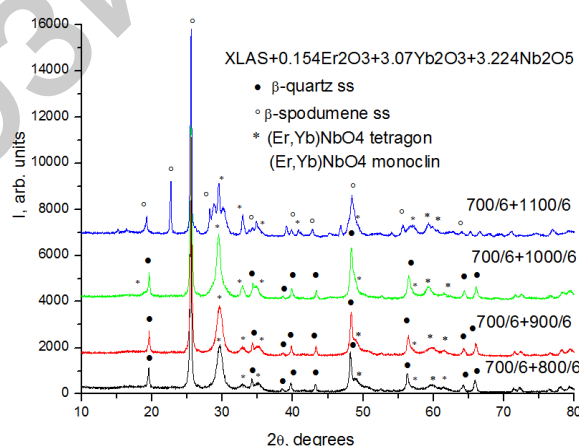


Fig. 1. X-ray diffraction of glass-ceramics

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}→²F_{5/2} transition of ytterbium ion and bands at 1450–1550 nm connected with ⁴I_{15/2}→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)NbO₄ nanocrystals (110–130 Å) with tetragonal structure.

Heat-treatment at 1000°C leads to a partial transformation of (Er,Yb)NbO₄ 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 Er³⁺ and Yb³⁺ ions do not enter its structure. This crystalline phase ensures high thermal shock resistance of the prepared materials.

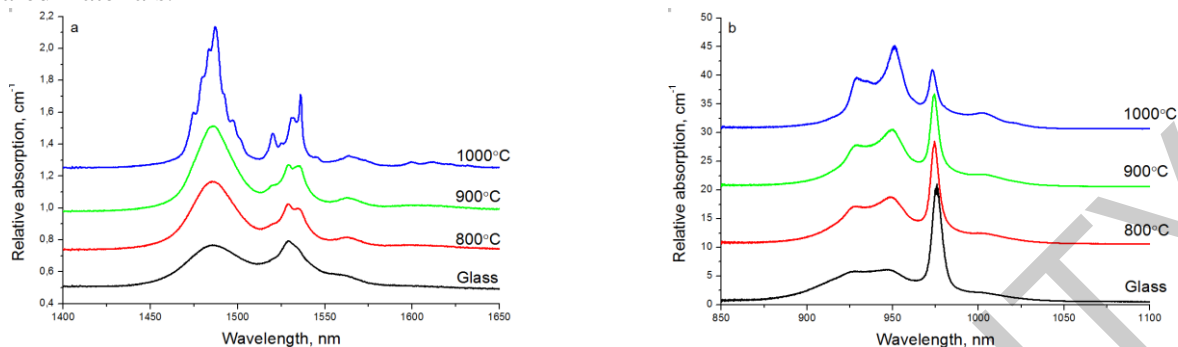


Fig. 2. Absorption spectra of Er³⁺ (a) and Yb³⁺ (b) ions in initial glass and glass-ceramics

Figure 3 presents up-conversion and near IR luminescence spectra of Er³⁺ ions in the initial glass and glass-ceramics. Luminescence bands in the green and red spectral ranges are attributed to transitions ²H_{11/2}→⁴I_{15/2} (near 522 nm) and ⁴S_{3/2}→⁴I_{15/2} (near 545 nm) of Er³⁺ 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 Er³⁺ ions is populated predominantly due to energy transfer from the Yb³⁺ ion excited state ²F_{5/2}. Luminescence spectra near 1.5 μm correspond to ⁴I_{13/2}→⁴I_{15/2} transition of Er³⁺ ions. Lifetime of Yb³⁺ ions in the ²F_{5/2} state (~3 μs) and Er³⁺ lifetimes in the ⁴I_{11/2} (~4-5 μs) and ⁴I_{13/2} states (~0,9-1 ms) have been obtained.

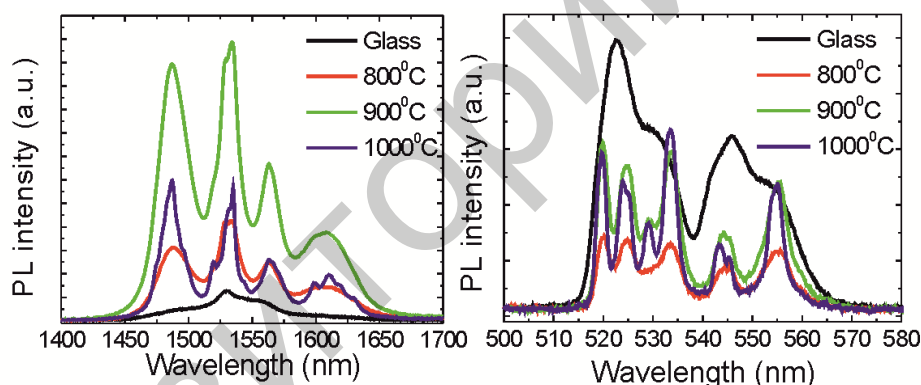


Fig. 3. IR and up-conversion luminescence spectra of Er³⁺ ions in the initial glass and glass-ceramics

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)NbO₄ nanocrystals and their partial recrystallization into monoclinic (Er,Yb)NbO₄ 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 ErYbNbO₄ 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.