Structural transformations and optical properties of glass-ceramics based on ZnO, β- and α-Zn2SiO4 nanocrystals and doped with Er2O3 and Yb2O3

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Abstract

Structural transformations in potassium-zinc-aluminosilicate glass codoped with Er2O3 and Yb2O3 and subjected to heat-treatments in the temperature range from 680 to 1300 ∘C were studied by differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. It was demonstrated that the structure of initial glasses depends on the concentration of the doping ions. The initial inhomogeneous glass contains either a small amount of ZnO nanocrystals of _˜10 nm in size located in the phase separated regions,or an amorphousor phase is RE-enriched. Transparent glass-ceramics based on nanosized ZnO crystals are prepared by heat-treatments in the temperature range of 700 – 800 ∘C. At elevated temperatures, in addition to ZnO nanosized crystals, β- and α-Zn2SiO4 (willemite), crystals precipitate and the material loses transparency. Crystallization of potassium aluminosilicates, leucite, KAlSi2O6, from the surface and calsilite, KAlSiO4 from the bulk is observed. Absorption and luminescence properties of the initial glass and GCs based on ZnO, β- and α-Zn2SiO4 (willemite) and RE silicate nanocrystals are reported. Strong near-IR absorption at the wavelengths longer than _˜1 μm was detected. The effect of the RE3+ ions on the appearance of this absorption is discussed; the possible reason is the formation of free charge carriers. Electron absorption and luminescence are assigned to certain crystals formation. In glass-ceramics, rare-earth (RE) ions are located in the residual glass phase until the heat-treatment temperature of 1200-1300 ∘C, when the crystals of RE2SiO5 are formed, which results in a pronounced enhancement and structuring of the Er3+ luminescence bands. This work was partly supported by the RFBR (Grant 16-03-01130). P.L. acknowledges financial support from the Government of the Russian Federation (Grant 074-U01) through ITMO Post-Doctoral Fellowship scheme.

Keywords: glass, ceramics, zinc oxide, willemite, X, ray diffraction, Raman spectroscopy, low, frequency Raman spectroscopy, luminescence

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