

Er-doped zinc-silicate glass-ceramics with enhanced emission in the near-infrared region

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Glass-ceramics from the system $A_2O-ZnO-SiO_2$ ($A = Li, Na, K, Cs$) were prepared, and the relationship between the composition, crystallization and luminescence properties is studied. The glass-ceramics contain various crystalline phases, including zinc oxide ZnO, zinc silicate Zn_2SiO_4 (willemite) or alkali zinc silicate A_2ZnSiO_4 . We show that the tendency towards crystallization increases with decreasing diameter of alkali cation, from Cs^+ to Li^+ . The Li_2O -containing glass crystallizes directly after melt-quenching, whereas the Cs_2O -containing glass only crystallizes after heat treatment at 900 °C. We show that the $Na_2O-ZnO-SiO_2$ system is highly beneficial for the crystallization of willemite. The presence of Zn_2SiO_4 nanocrystals in the Na_2O -containing samples is confirmed by TEM imaging, the size of nanocrystals is around 8 nm. The high crystallinity of the samples leads to a significant enhancement of emission intensity around 1.5 μm . However, the solubility of Er^{3+} ions in the zinc-based crystalline phases is shown to be highly limited. When heat treated in the range of 700 - 850 °C, the luminescence characteristics of the 1.5 μm emission, such as band shape or fluorescence lifetime remain nearly unchanged or exhibit only small modifications, suggesting negligible changes in the Er^{3+} environment. The Er^{3+} ions likely remain in the residual amorphous phase or grain boundaries. A significant evidence for the incorporation of Er^{3+} ions in crystalline lattice is observed only in samples heat treated at 900 °C, where the $Na_3ErSi_3O_9$ phase is formed in the $Na_2O-ZnO-SiO_2$ system.

This work was supported from the Specific university research – grant No. A1_FCHT_2022_008 and A2_FCHT_2022_048. This work was supported by the Czech Science Foundation, grant No. GA23-05507S