Effect of Ag co-doping on Pr^{3+} luminescence in lithium tetraborate glasses

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The spectroscopic and luminescent properties of the Pr-doped and Pr-Ag co-doped lithium tetraborate ($Li_2B_4O_7$ or $Li_2O–2B_2O_3$) glasses have been detailed studied using electron paramagnetic resonance (EPR), optical absorption, photoluminescence (emission, excitation, decay kinetics) and Judd–Ofelt analysis [1]. The optical absorption spectra of the investigated glasses show several $4f$ – $4f$ absorption bands related to Pr^{3+} ($4f^2$, $^3H_4$) ions. Co-doping with Ag leads to a significant increase of optical absorption in the visible and partly in the near infrared (NIR) regions due to effects of light scattering and surface plasmon resonance (SPR) absorption induced by silver nanoparticles.

The orange-red Pr^{3+} emission band with a maximum at 601 nm ($^1D_2 \rightarrow {}^3H_4$ transition) and a lifetime of 22 μs dominates in the luminescence spectra. An increase in the intensity of the Pr^{3+} luminescence in 40 % and 3 – 4 times upon excitation at 445 nm ($^3H_4 \rightarrow {}^3P_2$ transition) and at different photoexcitations in the UV region was observed in the $Li_2B_4O_7$:Pr,Ag glass in comparison with the $Li_2B_4O_7$:Pr glass. Based on the obtained experimental results and Judd–Ofelt theory, the experimental and theoretical oscillator strengths (f_{exp} and f_{theor}), phenomenological parameters (Ω_2, Ω_4, Ω_6), radiative properties (A_{rad}, β, τ_{rad}) and quantum efficiencies (η) of the Pr^{3+} luminescence were calculated.

The presence of isolated Ag^+ ($4d^{10}$, $^1S_0$) ions, small non-plasmonic Ag aggregates (Ag_m^{n+} nanoclusters) and plasmonic Ag metallic nanoparticles in the $Li_2B_4O_7$:Pr,Ag glass was proposed based on detailed analysis of optical absorption, photoluminescence spectra and decay curves. The observed enhancement of luminescence intensity as well as increase of stimulated emission cross-section and quantum efficiency of luminescence in the $Li_2B_4O_7$:Pr,Ag glass are explained by excitation energy transfer from Ag^+ ions and Ag aggregates to Pr^{3+} ions as well as local-field effect induced by Ag metallic nanoparticles. Silver co-doping is a promising approach to improve the luminescent properties of Pr^{3+} ions in borate glasses.

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