Optical and EPR spectroscopy of the $Li_2B_4O_7$:Cu,Eu and $Li_2B_4O_7$:Mn,Sm glasses (the review)

B. V. Padlyak[1,2#], I. I. Kindrat[1], A. Drzewiecki[1], V. T. Adamiv[2], I. M. Teslyuk[2]

[1]University of Zielona Góra, Institute of Physics, 4a Szafrana Str., 65-516 Zielona Góra, Poland
[2]Ivan Franko National University of Lviv, Vlokh Institute of Physical Optics, 23 Dragomanov Str., 79005 Lviv, Ukraine

The $Li_2B_4O_7$:Cu,Eu and $Li_2B_4O_7$:Mn,Sm glasses containing 1.0 mol.% CuO and Eu_2O_3 as well as 1.0 mol.% MnO_2 and Sm_2O_3, respectively were obtained and studied in details by XRD, EPR, optical absorption, and photoluminescence methods [1,2]. The studied glasses of high optical quality were obtained by high temperature melting technique. Parameters of the local structure (interatomic distances and coordination numbers) of the studied glasses were derived from XRD data analysis. The EPR and optical spectroscopy show that the Cu impurity is incorporated into the $Li_2B_4O_7$ glass network as Cu^{2+} ($3d^9$) and Cu^+ ($3d^{10}$) ions [1]. The Cu^{2+} ions in $Li_2B_4O_7$:Cu,Eu glass show characteristic EPR and optical absorption spectra. Spin Hamiltonian parameters of the Cu^{2+} EPR spectrum were determined . Optical band gap and Urbach energy of the $Li_2B_4O_7$:Cu,Eu glasses were evaluated. Photoluminescence spectra of the $Li_2B_4O_7$:Cu,Eu glass reveal broad blue emission band of the Cu^+ ($3d^94s^1 \rightarrow 3d^{10}$ transition) and narrow emission bands of the Eu^{3+} ($4f^6$) ions ($^5D_0 \rightarrow {}^7F_J$ (J = 0 – 4)) transitions with characteristic decay kinetics. Energy transfer processes $Eu^{3+} \rightarrow Cu^+$, Cu^{2+} and $Cu^+ \rightarrow Eu^{3+}$ in $Li_2B_4O_7$:Cu,Eu glass are considered.

The EPR and optical spectroscopy show the presence of Mn^{2+}($3d^5$) and Mn^{3+}($3d^4$) impurity ions in the $Li_2B_4O_7$:Mn,Sm glass [2]. By EPR spectroscopy in the studied glass were identified three types of Mn^{2+} centres: single Mn^{2+} (1) centres in the strongly distorted sites; single Mn^{2+} (2) centres in the sites with almost cubic symmetry; Mn^{2+} pairs and small clusters coupled by magnetic dipolar and exchange interactions. The Mn^{2+} EPR spectra parameters in the $Li_2B_4O_7$:Mn,Sm glass have been determined at T = 295 K. Optical absorption spectrum of the $Li_2B_4O_7$:Mn,Sm glass contains a very broad intense band peaked at 467 nm belonging to the $^5E_g(D) \rightarrow {}^5T_{2g}(D)$ transition of Mn^{3+} ions and several weak narrow lines corresponding to the $^6H_{5/2} \rightarrow {}^6P_{3/2}$, $^6H_{5/2} \rightarrow {}^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$ transitions of Sm^{3+} ($4f^5$, $^6H_{5/2}$) ions. Emission spectrum of the $Li_2B_4O_7$:Mn,Sm glass exhibits a broad band corresponding to the $^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ transition of Mn^{2+} ions and three characteristic bands in the yellow-orange-red range belonging to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ transitions of Sm^{3+} ions. Photoluminescence excitation and emission spectra and decay kinetics of Mn^{2+} and Sm^{3+} ions in the $Li_2B_4O_7$:Mn,Sm glass are interpreted. Energy transfer processes $Sm^{3+} \rightarrow Mn^{2+}$, Mn^{3+} and $Mn^{2+} \rightarrow Mn^{3+}$ in the studied glass are proposed.

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corresponding author: B.Padlyak@if.u.zgora.pl.