EPR SPECTROSCOPY OF THE Mn²⁺ AND Cu²⁺ CENTRES IN LITHIUM AND POTASSIUM-LITHIUM TETRABORATE GLASSES

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The Mn- and Cu-doped glasses with lithium and potassium-lithium tetraborate $(Li_2B_4O_7 \text{ and } KLiB_4O_7)$ compositions were obtained according to standard glass synthesis technology. For solid state synthesis of the $Li_2B_4O_7$ and $KLiB_4O_7$ compounds were used corresponding carbonates $(Li_2CO_3 \text{ and } K_2CO_3)$ and boric acid (H_3BO_3) of high chemical purity. All tetraborate glasses were obtained by fast cooling of the corresponding melt, heated more than 100 K higher that the melting temperature $(T_{melt} = 1190 \text{ and } 1080 \text{ K} \text{ for } Li_2B_4O_7 \text{ and } KLiB_4O_7 \text{ compounds, respectively})$ for exceeding of the glass transition point. The Mn and Cu impurities were added to the all $(Li_2B_4O_7 \text{ and } KLiB_4O_7)$ glass compositions in the form of CuO and MnO₂ oxide compounds in amount 0.4 mol. %.

The electron paramagnetic resonance (EPR) spectra of the Mn- and Cu-doped glasses with $Li_2B_4O_7$ and $KLiB_4O_7$ compositions were investigated and analysed. The EPR spectra were registered at room temperature with using commercial X-band spectrometer of the SE/X-2013 type, operating in the high-frequency (100 kHz) modulation mode of magnetic field. On the basis of obtained EPR spectra analysis it was shown that the Mn and Cu impurities are incorporated into the glass network as Mn^{2+} (${}^{6}S_{5/2}$ ground state, $3d^{5}$ electron configuration) and Cu^{2+} (${}^{2}D_{5/2}$, $3d^{9}$) ions. The observed EPR spectra of the Mn^{2+} and Cu^{2+} impurity centres are typical for glassy (or vitreous) state and are almost identical for glasses with $Li_2B_4O_7$ and $KLiB_4O_7$ compositions.

The Mn²⁺ EPR spectra in the glasses with Li₂B₄O₇ and KLiB₄O₇ compositions are characterized by following parameters, measured at T = 300 K: isotropic *g*-factor ($g_{iso} = 2.00 \pm 0.05$), isotropic hyperfine constant ($A_{iso} = (8.65 \pm 0.05)$ mT) and peak-to-peak linewidth of hyperfine components $\Delta B_{pp} = (3.50 \pm 0.05)$ mT.

The anisotropic Cu^{2+} EPR spectra in the glasses with $Li_2B_4O_7$ and $KLiB_4O_7$ compositions, registered at T = 300 K are characterized by the same *g*-values ($g_{\parallel} = 2.34 \pm 0.05$, $g_{\perp} = 2.06 \pm 0.05$) and peak-to-peak linewidth of hyperfine components ($\Delta B_{pp}^{\parallel} = (5.11 \pm 0.05) \text{ mT}$, $\Delta B_{pp}^{\perp} = (1.80 \pm 0.05) \text{ mT}$). The anisotropic hyperfine constants show some differences ($A_{\parallel} = (14.28 \pm 0.05) \text{ mT}$, $A_{\perp} = (2.34 \pm 0.05) \text{ mT}$ for glass with $Li_2B_4O_7$ composition and $A_{\parallel} = (14.21 \pm 0.05) \text{ mT}$, $A_{\perp} = (2.55 \pm 0.05) \text{ mT}$ for glass with $KLiB_4O_7$ composition).

The local structure of the Mn^{2+} and Cu^{2+} impurity centres in the lithium and potassium-lithium tetraborate glass network are discussed on the basis of obtained and referenced EPR and structural data for $Li_2B_4O_7$ and $KLiB_4O_7$ crystals and other borate glasses.