EPR SPECTROSCOPY OF THE Mn$^{2+}$ AND Cu$^{2+}$ 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$_2$B$_4$O$_7$ and KLiB$_4$O$_7$) compositions were obtained according to standard glass synthesis technology. For solid state synthesis of the Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ compounds were used corresponding carbonates (Li$_2$CO$_3$ and K$_2$CO$_3$) and boric acid (H$_3$BO$_3$) 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 ($T_{\text{melt}} = 1190$ and 1080 K for Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ compounds, respectively) for exceeding of the glass transition point. The Mn and Cu impurities were added to the all (Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$) glass compositions in the form of CuO and MnO$_2$ oxide compounds in amount 0.4 mol. %.

The electron paramagnetic resonance (EPR) spectra of the Mn- and Cu-doped glasses with Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ 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, 3$^d_5$ electron configuration) and Cu$^{2+}$ ($^2$D$_{5/2}$, 3$^d^9$) 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 CuO and MnO$_2$ oxide compounds in amount 0.4 mol. %.

The Mn$^{2+}$ EPR spectra in the glasses with Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ compositions are characterized by following parameters, measured at $T = 300$ K: isotropic g-factor ($g_{\text{iso}} = 2.00 \pm 0.05$), isotropic hyperfine constant ($A_{\text{iso}} = (8.65 \pm 0.05)$ mT) and peak-to-peak linewidth of hyperfine components $\Delta B_{\text{pp}} = (3.50 \pm 0.05)$ mT.

The anisotropic Cu$^{2+}$ EPR spectra in the glasses with Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ 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 $\Delta B_{\text{pp}}^\parallel = (5.11 \pm 0.05)$ mT, $\Delta B_{\text{pp}}^\perp = (1.80 \pm 0.05)$ mT). The anisotropic hyperfine constants show some differences ($A_{\parallel} = (14.28 \pm 0.05)$ mT, $A_{\perp} = (2.34 \pm 0.05)$ mT for glass with Li$_2$B$_4$O$_7$ composition and $A_{\parallel} = (14.21 \pm 0.05)$ mT, $A_{\perp} = (2.55 \pm 0.05)$ mT for glass with KLiB$_4$O$_7$ 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$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ crystals and other borate glasses.