EPR Spectroscopy of the Lithium Tetraborate Glasses Doped with Ag

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The X-band electron paramagnetic resonance (EPR) spectra of the Ag-doped borate glasses with $\text{Li}_2\text{B}_4\text{O}_7$ basic composition have been investigated and analysed. The $\text{Li}_2\text{B}_4\text{O}_7$:Ag glasses were obtained using standard glass synthesis and technological conditions described in [1]. The Ag impurity was introduced into the $\text{Li}_2\text{B}_4\text{O}_7$ composition as AgNO₃ compound and as metallic highly dispersed silver in amount 2.0 mol. %. By EPR spectroscopy it was shown that the Ag impurity is incorporated into the network of as-synthesised $\text{Li}_2\text{B}_4\text{O}_7$ glasses as the Ag²⁺ (4d⁹) paramagnetic ions. The observed broad asymmetric EPR signal with the effective g-factor $g_{\text{eff}} = 2.05 \pm 0.01$ at room temperature is typical for highly Ag-doped glasses [2,3] and is associated with Ag^{2+} ions that are coupled by magnetic dipolar interaction. In all investigated $\text{Li}_2\text{B}_4\text{O}_7$:Ag glasses also clearly has been observed the characteristic for glasses EPR signal with $g_{\text{eff}} \cong 4.29$ that belongs to the Fe³⁺ non-controlled impurity ions.

Thermal annealing of the Li₂B₄O₇:Ag glasses in the air atmosphere at temperature 710 K during 2 hrs leads to complete disappearing of the Ag²⁺ EPR signal, whereas the effective g - factor, integral intensity, and peak-to-peak derivative linewidth of the Fe³⁺ EPR signal practically were not change after this oxidising annealing.

As-synthesised $Li_2B_4O_7$: Ag glasses were annealed at temperature 710 K during 4 hrs in the reducing H_2 atmosphere (gas pressure 700 mm Hg) and in vacuum (10^{-4} Torr with titanium getter) for formation in them of a near-surface layer, containing the Ag nanoparticles [4,5]. The EPR spectroscopy shows complete disappearing of the Ag^{2+} signal in the $Li_2B_4O_7$: Ag glasses, annealed in the H_2 atmosphere and vacuum and practically unchanged parameters of the Fe³⁺ signal after the reducing annealing.

Optical properties of the $Li_2B_4O_7$ glasses and parameters of the metallic silver (Ag) nanoparticles in them, obtained by reducing thermal annealing were described in [4,5]. The obtained results of EPR spectroscopy and published data in [4,5] are discussed in the terms of redox processes, which take place in the $Li_2B_4O_7$:Ag glasses during thermal annealing in the oxidising (air) and reducing (H₂ and vacuum) atmospheres.

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