Multivalence states of Mn and Yb ions in Li$_2$B$_4$O$_7$ single crystals and glasses

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Single crystals of Li$_2$B$_4$O$_7$ doped with Mn$^{2+}$ (0.014 mol. %), Yb$^{3+}$ (1 mol. %) and Li$_2$B$_4$O$_7$ glasses doped with Mn$^{2+}$ (0.1 mol. %) and Yb$^{3+}$ (1 mol. %), have been investigated using EPR method at 9.4 GHz. In both systems both Mn$^{2+}$ and Yb$^{3+}$ ions are found enter substantially for the Li$^+$ ions as Mn$^{2+}$, Mn$^{1+}$ and Yb$^{3+}$, and, probably for the B$^{4+}$ ion or interstitial.

In case of Mn-doped systems at least two types of manganese ions arise in the EPR spectrum in the same range of magnetic field. The EPR spectrum of glass system exhibits three resonance signals, at $g$~2.00, $g$~2.68 and $g$~4.60 and is very similar to others reported for Mn$^{2+}$ ions glass systems. The EPR spectrum of Li$_2$B$_4$O$_7$:Mn crystal reveals only $g$~2.00 and $g$~2.89 lines. Annealing in Ar atmosphere does not change the spectrum ($g$=1.97(8)) while irradiation with $\gamma$-quanta with a dose of 5*10$^4$ Gy decreases to some extent the intensity of Mn$^{2+}$ EPR signal ($g$=1.99±0.01) introducing new EPR line ($g$=2.14±0.01), giving evidence on formation of other (Mn$^{1+}$, Mn$^{6+}$, Mn$^{0}$) valence states of manganese, moreover, F-type and/or V$_k$ color centers are formed.

The optical investigations of “as-grown” and $\gamma$-irradiated samples were performed giving evidence on Mn$^{0}$, Mn$^{6+}$ and Yb$^{2+}$ formation in the crystal after $\gamma$-irradiation.

In case of Mn-doped glass and crystal only the 430 and 620 nm emission was observed in photoluminescence and/or radioluminescence spectra, while also 530 emission in the glass irradiated with gamma quanta. TL measurements of the Mn-doped crystal reveal the strong TL peak at about 95 K, assigned probably to F$^+$ center.

Keywords: lithium tetraborate, photoluminescence, EPR, induced absorption