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EPR Spectroscopy of the Mn^{2+} and Cu^{2+} Centres in Lithium and Potassium–Lithium Tetraborate Glasses

B.V. Padlyak[a,b,*], W. Wojtowicz[b], V.T. Adamiv[a], Ya.V. Burak[a] and I.M. Teslyuk[a]

[a]Institute of Physical Optics, 23 Dragomanov Str., 79-005 Lviv, Ukraine

[b]Institute of Physics, University of Zielona Góra, 4a Szafrana Str., 65-516 Zielona Góra, Poland

The electron paramagnetic resonance spectra of the glasses with $Li_2B_4O_7$ and $KLiB_4O_7$ compositions doped with Mn and Cu were investigated. 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+} ($^6S_{5/2}$, $3d^5$) and Cu^{2+} ($^2D_{5/2}$, $3d^9$) ions. The Mn^{2+} EPR spectra in the glasses with $Li_2B_4O_7$ and $KLiB_4O_7$ compositions are characterised by the 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 Cu^{2+} EPR spectra in the glasses with $Li_2B_4O_7$ and $KLiB_4O_7$ compositions, registered at $T = 300$ K are characterised by the same g-values ($g_{\parallel} = 2.34 \pm 0.05$, $g_{\perp} = 2.06 \pm 0.05$) and peak-to-peak line width of hyperfine components ($\Delta B^{\parallel}_{\text{pp}} = (5.11 \pm 0.05)$ mT, $\Delta B^{\perp}_{\text{pp}} = (1.80 \pm 0.05)$ mT), whereas 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 $Li_2B_4O_7$ composition and $A_{\parallel} = (14.21 \pm 0.05)$ mT, $A_{\perp} = (2.55 \pm 0.05)$ mT for glass with $KLiB_4O_7$ composition). The possible local structure of the Mn^{2+} and Cu^{2+} centres in the lithium and potassium–lithium tetraborate glass network has been considered.

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1. Introduction

The borate, in particular, tetraborate crystals are characterized by extremely high radiation stability [1, 2] and transparency in the wide spectral range from VUV to far IR. In connection with their attractive properties, the undoped and doped tetraborate compounds are promising materials for different technical applications: scintillators and tissue-equivalent materials for thermoluminescence (TL) dosimetry [3–5], γ and neutron detectors [6, 7] and others.

The obtaining of tetraborate single crystals is technologically difficult, long-term and, in consequence, very expensive. Beside this, very low velocity of the crystals growth and high viscosity of the melt leads to difficulties with doping of tetraborate crystals. Therefore, from the technological point of view the glassy (or vitreous) borate compounds are most perspective in comparison with their crystalline analogies. On the other side, the study of electron and local structure of the intrinsic, impurity and radiation-induced point defects in the complex oxide glasses is interesting problem of solid state physics. Therefore, the synthesis and spectroscopic investigation of the doped borate glasses with different basic compositions, in particular with $Li_2B_4O_7$ (LTB) and $KLiB_4O_7$ (KLTB) one, is very important from the practical application and fundamental points of view.

The electron paramagnetic resonance (EPR) spectroscopy allows investigating the electron and local structure of the impurity and radiation-induced point defects in crystals and corresponding glasses. Interpretation of the EPR and optical spectra in complex glasses and derivation of the electron and local structure of point defects from experimental spectra require the structural and EPR data for their crystalline analogies [8, 9]. Practically, all borate compounds, including tetraborates, can be obtained in both crystalline and glassy states and, therefore, are good candidates for study of the nature of point defects in them.

The LTB crystals and glasses doped with Mn and Cu at present time are widely investigated by optical spectroscopy [10–14]. Particularly, it was shown by optical spectroscopy [10] that for "as-grown" non-irradiated LTB:Cu and LTB:Mn crystals the multivalent states of dopants are characteristic and Mn impurity reveals as Mn^{2+} and Mn^{3+} ions and Cu impurity reveals as Cu^{+} and Cu^{2+} ions. The EPR spectra of the Mn^{2+} ions in LTB crystals and glasses were presented and described for the first time in [13]. The Mn^{2+} spin Hamiltonian parameters in the LTB crystals were determined at 77 and 300 K and local structure of the Mn^{2+} centres in the LTB crystal and glass was discussed in [13]. Firstly in Ref. [14] there were presented, typical for crystalline and

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[*] corresponding author; e-mail:
`B. Padlyak@proton.if.uz.zgora.pl`, `bohdan@mail.lviv.ua`

glassy oxide compounds, EPR spectra of the Cu^{2+} ions in the LTB crystal and glass at different temperatures, but spin Hamiltonian parameters and local structure of the Cu^{2+} centres were not determined.

As we can see from referenced data the EPR spectra of LTB glasses doped with Mn and Cu were studied insufficiently. Moreover, the EPR spectra of new crystals and glasses with KLiB$_4$O$_7$ composition doped with Mn and Cu were not investigated up to now. Therefore, the presented work is devoted to EPR investigation of the LTB and KLTB glasses doped with Mn and Cu and to determination of electron and local structure of paramagnetic centres in the glass network based on the obtained and referenced EPR and structural data for corresponding tetraborate crystals and glasses.

2. Experimental details

The LTB and KLTB glasses doped with Mn and Cu were obtained from corresponding polycrystalline compounds according to standard glass technology. For solid state synthesis of the Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ compounds we used corresponding carbonates (Li$_2$CO$_3$ and K$_2$CO$_3$) and boric acid (H$_3$BO$_3$) of high chemical purity (99.999%). All tetraborate glasses were obtained by fast cooling of the corresponding melted compounds, heated more than 100 K higher than their melting temperature ($T_{\text{melt}} = 1190$ and 1080 K for LTB and KLTB compounds, respectively) for exceeding of the glass transition point. The Mn and Cu impurities were added to the LTB and KLTB compositions in the form of CuO and MnO$_2$ oxide compounds in amount 0.4 mol%.

The EPR spectra were registered at room temperature with using modernised commercial X-band spectrometer of the SE/X-2013 type ("RADIOPAN", Poznań, Poland), operating in the high-frequency (100 kHz) modulation mode of magnetic field. The microwave frequency were measured with the use of the Hewlett Packard microwave frequency counter of the 5350 B type and DPPH g-marker ($g = 2.0036 \pm 0.0001$). The parameters of registered EPR spectra were obtained with using computer analysis of the obtained experimental spectra.

3. Results and discussion

In all LTB and KLTB glasses doped with Mn and Cu at room temperature there were registered EPR spectra typical for glassy compounds, and are presented in Figs. 1 and 2.

3.1. EPR spectra of the non-controlled impurities in tetraborate glasses

In the LTB and KLTB glasses doped with Mn and Cu there were observed two characteristic EPR signals with $g_{\text{eff}} = 4.29 \pm 0.01$ and $g_{\text{eff}} = 2.00 \pm 0.01$ (Figs. 1 and 2). These signals were observed also in all undoped and rare-earth doped glasses with Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ compositions. In the investigated glasses integral intensity of the signal with $g \approx 4.29$ is more than 100 times greater than the $g \approx 2.00$ one. Both observed signals belong to non-controlled Fe^{3+} ($^6S_{5/2}$, $3d^5$) impurity ions.

The first explanation of the signal at $g_{\text{eff}} \approx 4.29$ in the glass network was proposed by Castner et al. [15] on the basis of spin Hamiltonian in the form given by Bleaney and Stevens [16]:

$$\hat{H} = \beta\left(\boldsymbol{B} g \hat{\boldsymbol{S}}\right) + D\left[S_z^2 - (1/3)S(S+1)\right] + E\left(S_x^2 - S_y^2\right), \qquad (1)$$

where D and E are the axial and orthorhombic crystal field terms, respectively. At present time it is generally acknowledged [17] that the signal at $g_{\text{eff}} \approx 4.29$ originates from isolated $3d^5$-ions (Fe^{3+} and Mn^{2+}) for large second-order ligand field splitting in which the value of ratio $|E/D|$ lies in the vicinity of its maximum value of 1/3 (for fully rhombic symmetry $|E/D| = 1/3$). Several types of fully rhombic distortions of the sixfold (octahedral) and fourfold (tetrahedral) oxygen coordinated sites were considered in [18]. According to [18], EPR signals with $g_{\text{eff}} \approx 4.29$ in the LTB and KLTB glasses can be assigned to isolated Fe^{3+} ions in octahedrally- and (or) tetrahedrally-coordinated sites of the tetraborate glass network with a strong rhombic distortion.

The EPR signal with $g \approx 2.00$ is characteristic for Fe^{3+} ions in crystals and, besides the signal with $g_{\text{eff}} \approx 4.29$, it was observed also in number glasses, particularly in the borate and phosphate glasses even at very low iron concentration [17]. By computer simulation in [19] it was shown that the weak EPR line with $g \approx 2.00$ in borate glasses belongs to isolated Fe^{3+} ions, localised in sites with nearly cubic symmetry. One can notice that the presence of dominated Fe^{3+} signal with $g \approx 4.29$ clearly demonstrating the classical glass structure of investigated samples.

In the LTB and KLTB glasses doped with Mn there was observed also weak EPR signal with $g \approx 1.97$ (Fig. 1A, B), which according to [8] belongs to Cr^{3+} ($3d^3$, $^2D_{3/2}$) ions with large axial ($D > g\beta B$) and small orthorhombic ($|E/D| \ll 1$) crystal field parameters.

3.2. The Mn^{2+} impurity centres

The EPR spectra of the LTB and KLTB glasses doped with Mn are presented in Fig. 1A, B. The observed spectra consist of a broad absorption band centred near $g \approx 4.29$, a distinct "shoulder" at $g \approx 3.3$ and intense broad band ($\Delta B_{\text{pp}} \approx 50$ mT) centred at $g = 2.00$ with the six equidistant well-resolved hyperfine components, caused by the ^{55}Mn isotope nuclei (natural abundance — 100%, nuclear spin $I = 5/2$). As we can see from Fig. 1, the observed EPR spectra are virtually identical for glasses with LTB:Mn and KLTB:Mn compositions and are typical for glassy compounds doped with Mn [8, 17, 20]. One can notice that the similar EPR spectra in the LTB:Mn glasses were observed in [13]. This kind of EPR spectra is characteristic for a number of differ-

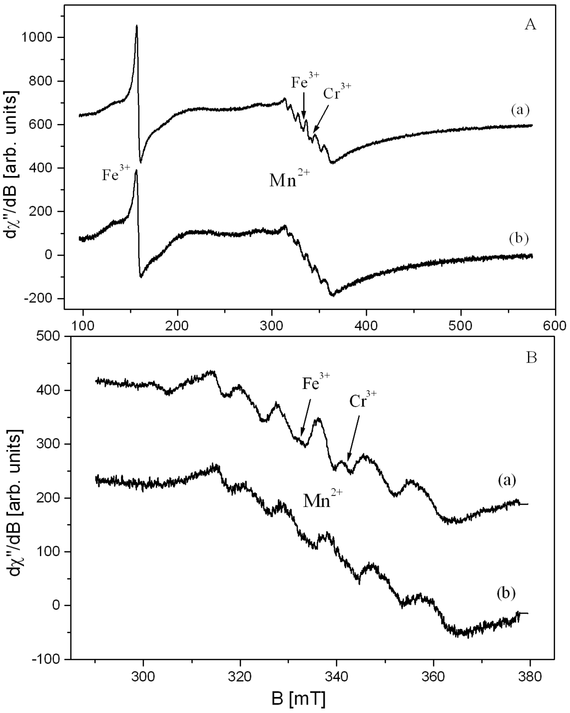

Fig. 1. The complete (A) and central part (B) of X-band EPR spectra of the LTB (a) and KLTB (b) glasses doped with Mn, registered at $T = 300$ K.

ent oxide glasses, doped with manganese and belongs to isolated Mn^{2+} ($^6S_{5/2}$, $3d^5$) ions.

The observed Mn^{2+} EPR spectra in glasses with LTB:Mn and KLTB:Mn compositions are characterised by the following parameters, measured at $T = 300$ K: isotropic g-factor ($g_{\rm iso} = 2.00 \pm 0.05$), isotropic hyperfine constant of the ^{55}Mn isotope ($A_{\rm iso} = (8.65 \pm 0.5)$ mT) and peak-to-peak linewidth of hyperfine components $\Delta B_{\rm pp} = (3.50 \pm 0.05)$ mT. The Mn^{2+} EPR spectra in tetraborate glasses (Fig. 1) are practically independent of temperature and composition of the glass matrix.

The local structure and crystal field parameters (D and E) of the Mn^{2+} centres in oxide glasses have been the subject of considerable discussions in literature [8, 17, 18, 20]. According to interpretation, given in [17, 18], we can conclude that the isolated Mn^{2+} centres occupy structural sites with strongly distorted rhombic (signal with $g_{\rm eff} = 4.29$) and nearly cubic (signal with $g_{\rm eff} = 2.00$) symmetry, which are characterised by a broad distribution of crystal field parameters. Most probably Mn^{2+} ions occupy strongly distorted tetrahedral or octahedral Li (K) sites in the tetraborate glass network.

The Mn^{2+} EPR spectra in all tetraborate glasses have a broad unresolved underlying response centred at $g = 2.00$ (Fig. 1), which according to referenced data [8, 17, 21] can be attributed to the Mn^{2+} exchange-coupled pairs and clusters. Therefore, the Mn is incorporated into tetraborate glass network as isolated Mn^{2+} ions in the strongly distorted and nearly cubic tetrahedral or octahedral sites and exchange-coupled Mn^{2+} pairs and small clusters.

3.3. The Cu^{2+} impurity centres

The EPR spectra of the LTB and KLTB glasses doped with Cu are presented in Fig. 2A, B. In both tetraborate glasses EPR spectra are quite similar and consist of pronounced band centred at $g = 2.34$ with weakly-resolved four-component structure and a relatively shallow quadruplet, centred at $g = 2.06$ (Fig. 2A, B). Both observed signals belong to Cu^{2+} ($^2D_{5/2}$, $3d^9$) ions. Four weakly-resolved components related to hyperfine structure, caused by the ^{63}Cu and ^{65}Cu isotopes nuclei (natural abundance — 69.1% of ^{63}Cu and 30.9% of ^{65}Cu, nuclear spin $I = 3/2$ for both isotopes). The hyperfine components belonging to the ^{63}Cu and ^{65}Cu isotopes are not resolved in the observed EPR spectra, because their nuclear magnetic moments are closely similar (nuclear magnetic moment is 7.1% higher for ^{65}Cu than that for ^{63}Cu one).

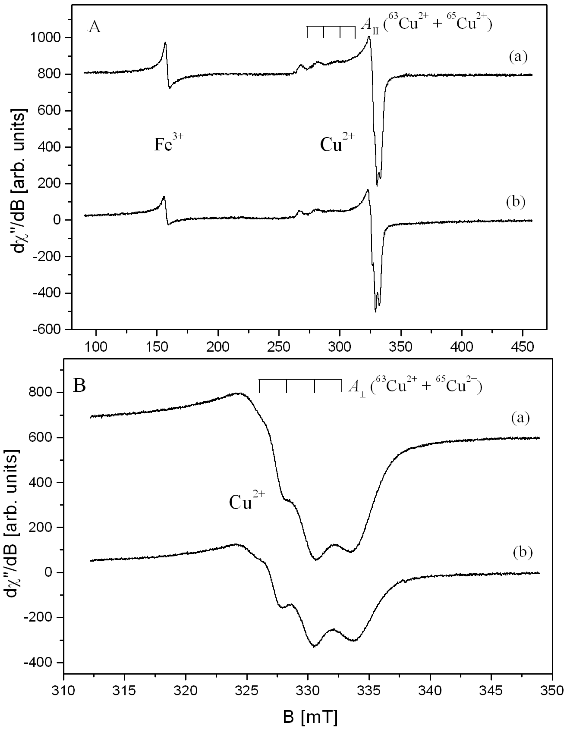

Fig. 2. The complete (A) and central part (B) of X-band EPR spectra of the LTB (a) and KLTB (b) glasses doped with Cu, registered at $T = 300$ K.

The observed Cu^{2+} EPR spectra in the glasses with Li$_2$B$_4$O$_7$ and KLiB$_4$O$_7$ compositions can be described by the spin Hamiltonian of axial symmetry in the form

$$\hat{H} = g_{\parallel}\beta B_z \hat{S}_z + g_{\perp}\beta \left(B_x \hat{S}_x + B_y \hat{S}_y\right) + A_{\parallel}\hat{S}_z \hat{I}_z + A_{\perp}\left(\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y\right) \qquad (2)$$

with the following parameters, determined at $T = 300$ K:

$g_{\|} = 2.34 \pm 0.05$, $g_{\perp} = 2.06 \pm 0.05$, $A_{\|} = (14.28 \pm 0.05)$ mT, $A_{\perp} = (2.34 \pm 0.05)$ mT (for LTB glass) and $A_{\|} = (14.21 \pm 0.05)$ mT, $A_{\perp} = (2.55 \pm 0.05)$ mT (for KLTB glass). The peak-to-peak line width of hyperfine components for LTB:Cu and KLTB:Cu glasses at $T = 300$ K equals: $\Delta B_{\mathrm{pp}}^{\|} = (5.11 \pm 0.05)$ mT, $\Delta B_{\mathrm{pp}}^{\perp} = (1.80 \pm 0.05)$ mT.

The observed $g_{\|}$ and $g_{\perp}$ values are characteristic of a $3d^9$ Jahn–Teller ions coordinated by six O^{2-} ligands that form an oxygen octahedron, elongated along the z-axis. The ground state for unpaired electrons is $^2B_{1\mathrm{g}}$ (d_{x2-y2} orbital) because $g_{\|} > g_{\perp} > g_{\mathrm{e}} = 2.0023$ [20, 22]. Some differences in hyperfine constants for Cu^{2+} centres in LTB and KLTB glass network can be related to slightly different local environments in their second coordination sphere. The Cu^{2+} similar as Mn^{2+} impurity centres are incorporated into the Li (or K) sites of the LTB and KLTB glass network with coordination number to oxygen $N = 4 \div 6$, because local environments in glasses are closely similar to corresponding crystals [23, 24].

4. Conclusions

On the basis of obtained and referenced EPR and structural data analysis the following was shown:

1) The Mn and Cu impurities are incorporated into the LTB and KLTB glass network in the Mn^{2+} ($3d^5$, $^6S_{5/2}$) and Cu^{2+} ($^2D_{5/2}$, $3d^9$) valence state and their EPR spectra are practically independent of composition of the tetraborate glass matrix.

2) The isotropic Mn^{2+} centres in the LTB and KLTB glasses are characterised by, typical for glassy state, EPR spectra, which are independent of the basic glass composition and temperature in the 77–300 K range. Parameters of the Mn^{2+} EPR spectra for LTB:Mn and KLTB:Mn glasses were obtained at $T = 300$ K.

3) The EPR spectra of the Cu^{2+} centres in the LTB:Cu and KLTB:Cu glasses were observed and analysed and their parameters were obtained at $T = 300$ K.

4) The Mn^{2+} and Cu^{2+} impurity ions are incorporated into the Li (or K) sites of the tetraborate glass structure with coordination number to oxygen $N = 4 \div 6$. The charge compensation mechanism for $Mn^{2+} \rightarrow Li^+$ (or K^+) and $Cu^{2+} \rightarrow Li^+$ (or K^+) heterovalence substitutions can be connected with Li (or K) vacancies in glass network.

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