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EPR SPECTROSCOPY OF TETRABORATE GLASSES, DOPED WITH Mn AND Cu

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The X-band EPR spectra of tetraborate glasses with $Li_2B_4O_7$ and $KLiB_4O_7$ chemical compositions, doped with Mn and Cu in different concentration were investigated. On the basis of obtained data analysis it was shown that the Mn and Cu are incorporated into the tetraborate glass network as Mn^{2+} ($3d^5$, $^6S_{5/2}$) and Cu^{2+} ($3d^9$, $^2D_{5/2}$) ions and their EPR spectra are characteristic for glassy compounds. The Mn^{2+} ions are incorporated into the tetraborate glass network as isolated centres and small exchange-coupled clusters for low and high Mn concentration, whereas the Cu^{2+} ions are incorporated into the glass structure as isolated centres, exclusively. The parameters of the Mn^{2+} and Cu^{2+} activator as well as Fe^{3+} non-controlled impurity centres in both tetraborate glasses with amounts 0.4 and 1.6 mol.% of the MnO_2 and CuO doping compounds were determined at T = 300 K. The obtained *g*-factor and hyperfine constant values are practically independent of the basic composition of tetraborate glasses and impurities concentration in them. The increasing of dopant concentration leads to homogeneous broadening of EPR lines of the Mn^{2+}, Cu^{2+} and Fe^{3+} centres, caused by magnetic dipole-dipole interaction.

INTRODUCTION

Un-doped and doped tetraborate crystals are known to have attractive properties and are widely used for the production of scintillators, tissue-equivalent materials for thermoluminescence (TL) dosimeters (Santiago M., Lester M., Caselli E. & Lavat A., 1998; Prokic M., 2002; Can N., Karali T., Townsend P. D. & Vildiz D. F., 2006), γ and neutron detectors (Senguttuvan N., Ishii M., Shimoyama M., Kobayashi M., Tsutsui N., Nikl M., Dusek M., Shimizu H. M., Oku T., Adachi T., Sakai K. & Suzuki J., 2002; Zadneprowski B. I., Eremin N. E. & Paskhalov A. A., 2005), *etc*. Because of technological difficulties in production of tetraborate single crystals, easily obtained glassy (or vitreous) analogies of borate compounds are more popular.

Investigations of electron structure, local environment and crystal field parameters of transitional and rare-earth metals impurity ions in disordered crystalline and glassy systems are current topics of solid state physics. As almost all borates can be obtained in both crystalline and glassy states, it is interesting to investigate electron and local structure of impurity point defects in crystals and corresponding glasses by EPR and optical spectroscopy.

In recent years such compounds as $Li_2B_4O_7$ (LTB) crystals and glasses doped with copper and manganese have drawn much attention and have been thoroughly investigated, in general, by means of optical spectroscopy (Ignatovych M., Holovey V., Watterich A., Vidóczy T., Baranyai P., Kelemen A., Ogenko V. & Chuiko O., 2003; Podgórska D., Kaczmarek S. M., Drozdowski W., Wabia M., Kwasny M., Warchol S. & Rizak V. M., 2004; Ignatovych M., Holovey V., Vidóczy T., Baranyai P., Keleman A., Laguta V. & Chujko O., 2005; Ignatovych M., Holovey V., Vidóczy T., Baranyai P. & Kelemen A., 2007). Results of these investigations showed that the LTB:Cu and LTB:Mn crystals are characterized by multivalent states of dopants. As a result the Mn and Cu impurities reveal themselves as Mn^{2+}, Mn^{3+} and Cu^{+}, Cu^{2+} ions.

Original results of EPR investigations of Mn^{2+} and Cu^{2+} centres in LTB crystals and glasses were reported in (Podgórska D. *et al.*, 2004; Ignatovych M., *et al.*, 2005; Padlyak B. V., Wojtowicz W., Adamiv V. T., Burak Ya.V. & Teslyuk I. M., 2010). The present work dwells upon the results of recent investigation of Mn^{2+} and Cu^{2+} centres in the LTB and $KLiB_4O_7$ (KLTB) glassy matrices. The dependencies of EPR spectra parameters of the impurity paramagnetic centres in the LTB:Mn, KLTB:Mn, LTB:Cu and KLTB:Cu glasses on the dopant concentration are considered and discussed.

EXPERIMENTAL

The LTB and KLTB glasses of high optical quality and chemical purity doped with copper and manganese were obtained from the corresponding polycrystalline compounds by the high-temperature synthesis method. The melt of boric acid (H_3BO_3), Li_2CO_3 for the synthesis of the LTB glass and additionally of K_2CO_3 for the synthesis of the KLTB glass was quickly cooled down starting from temperature 100 K above the melting point. Copper and manganese impurities were added to the melt as a CuO and MnO_2 oxide compounds in the amount of 0.4 and 1.6 mol.%.

For EPR spectra registration was used modernized commercial X-band spectrometer of the SE/X-2013 type ("RADIOPAN", Poznań, Poland). The microwave frequency was measured by the Hewlett Packard microwave frequency meter of the 5350 B type.

RESULTS AND DISCUSSION

EPR spectra of LTB and KLTB glasses, doped with Mn and Cu are presented in Figs. 1 - 2. Obtained EPR spectra are typical for glasses and practically independent of temperature in the 77 – 300 K range.

Table 1. The parameters of EPR signals of the Fe^{3+} centres in tetraborate glasses

Glass composition	Impurity amount (mol.%)	g-factor value	EPR linewidth, ΔH_{pp} (mT)
$Li_2B_4O_7$:Cu	0.4	4.28 ± 0.05	4.14 ± 0.05
	1.6	4.28 ± 0.05	4.23 ± 0.05
$KLiB_4O_7$:Cu	0.4	4.29 ± 0.05	3.68 ± 0.05
	1.6	4.29 ± 0.05	4.02 ± 0.05
$Li_2B_4O_7$:Mn	0.4	4.30 ± 0.05	4.26 ± 0.05
	1.6	4.27 ± 0.05	5.80 ± 0.05
$KLiB_4O_7$:Mn	0.4	4.32 ± 0.05	6.18 ± 0.05
	1.6	4.27 ± 0.05	6.24 ± 0.05

EPR signals of non-controlled paramagnetic impurities in the LTB and KLTB glasses

In all LTB and KLTB glasses, doped with Mn and Cu an EPR line cantered at $g_{eff} = 4.29 \pm 0.01$ was registered (Figs. 1 – 2, left side). It is generally acknowledged (Griscom D. L., 1980; Brodbeck C. M. & Bukrey R. R., 1981; Padlyak B.V. & Gutsze A., 1998) that this isotropic EPR signal can be attributed to Fe^{3+} ($3d^5$, $^6S_{5/2}$) impurity ions. One should note that the presence of the intensive Fe^{3+} signal with $g_{eff} = 4.29 \pm 0.01$ is an attribute of the classical glass structure of investigated samples (Castner T., Newell G. S., Holton W. C. & Slichter C. P., 1960; Griscom D. L., 1980; Brodbeck C. M. & Bukrey R. R., 1981; Padlyak B.V. & Gutsze A., 1998; Padlyak B. *et al.*, 2010). Table 1 demonstrates dependencies of the Fe^{3+} EPR signal parameters (g-factor and peak-to-peak derivative linewidth, ΔH_{pp}, values) on the tetraborate glass composition ($Li_2B_4O_7$ and $KLiB_4O_7$) and impurity (Cu and Mn) concentration.

As it can be seen from Table 1, the Fe^{3+} EPR signal broadens with the increase of the Cu and Mn impurities concentration in the LTB and KLTB glasses. Thus it can be concluded that the impurity compounds, such as CuO, Mn_2O, but not basic ones (H_3BO_3, $Li_2C_4O_3$, K_2CO_3), are the source of Fe^{3+} non-controlled impurity ions in doped tetraborate glasses.

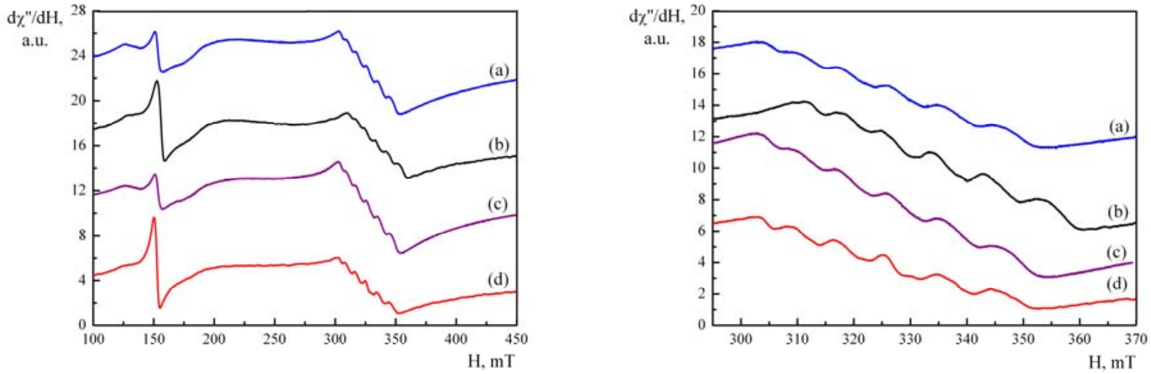

Fig. 1. The room temperature EPR spectra of the LTB:Mn (a, b) and KLTB:Mn (c, d) glasses, containing 0.4 mol.% (b, d) and 1.6 mol.% (a, c) of the MnO_2 compound. Left side – complete EPR spectra, right side – central part of the EPR spectra. Spectrum (b) was recorded at microwave frequency ν = 9.44 GHz and the other spectra were recorded at ν = 9.2 GHz.

One can notice that in some LTB and KLTB glasses, doped with Mn a weak EPR line centred at $g = 1.97$ was observed. The signal at $g = 1.97$ can be attributed to Cr^{3+} ($3d^3$, $^2D_{3/2}$) non-controlled impurity ions with large axial D ($D > g\beta H$) and small orthorhombic E ($|E/D| << 1/3$) values of the spin Hamiltonian parameters (Padlyak B.V. & Gutsze A., 1998; Padlyak B. *et al.*, 2010).

EPR spectra of the Mn^{2+} impurity centres in glasses with LTB and KLTB compositions

EPR spectra of the Mn^{2+} ($3d^5$, $^6S_{5/2}$) impurity centres in the LTB and KLTB glasses with different manganese concentrations are presented in Fig. 1.

As one can see from Fig. 1, the EPR spectra of Mn^{2+} centres are almost identical for the LTB and KLTB glassy matrices and consist of broad signal centred at $g \approx 4.29$ and an intense broad ($\Delta H_{pp} \approx 50$ mT) signal centred near $g = 2.00$ with six almost equidistant well-resolved hyperfine (HF) components. The presence of HF components is caused by the ^{55}Mn isotope nuclei (natural abundance – 100 %, nuclear spin $I = 5/2$).

As one can be seen from Table 2, the increase of Mn concentration results in greater values of EPR linewidth, caused by homogeneous broadening, while the g-factor (g_{iso}) and HF constant (A_{iso}) values are practically independent (in the framework of experimental errors) on the glass composition or on the Mn impurity concentration.

Table 2. The parameters of EPR spectra of the Mn^{2+} centres in tetraborate glasses

Glass composition	MnO_2 amount (mol.%)	g_{iso}	A_{iso} (mT)	ΔH_{iso} (mT)
$Li_2B_4O_7$:Mn	0.4	2.01 ± 0.05	8.67 ± 0.05	6.77 ± 0.05
	1.6	2.00 ± 0.05	8.67 ± 0.05	6.61 ± 0.05
$KLiB_4O_7$:Mn	0.4	2.03 ± 0.05	8.77 ± 0.05	6.74 ± 0.05
	1.6	1.98 ± 0.05	8.84 ± 0.05	7.45 ± 0.05

Taking into account the interpretation based on the analysis of the spin Hamiltonian parameters and local structure given in (Padlyak B.V. & Gutsze A., 1998; Padlyak B. *et al.*, 2010), we can conclude that the isolated Mn^{2+} centres occupy structural sites with strongly distorted rhombic (signal with $g_{eff} = 4.29$) and nearly cubic (signal with $g_{eff} = 2.00$) symmetry. Most probably the Mn^{2+} ions occupy strongly distorted tetrahedral or octahedral Li (K) sites in the tetraborate glass network.

According to the analysis, given in (Burzo E. & Ardelean I., 1978; Padlyak B.V. & Gutsze A., 1998; Padlyak B. *et al.*, 2010), a broad unresolved response centred at $g = 2.00$ can be attributed to the Mn^{2+} exchange-coupled pairs and small (more than two) clusters.

EPR spectra of the Cu^{2+} impurity centres in glasses with LTB and KLTB compositions

The EPR spectra of Cu^{2+} ($3d^9$, $^2D_{5/2}$) impurity centres in the LTB:Cu and KLTB:Cu glasses, containing different amount of the CuO, registered at room temperature are presented in Fig. 2.

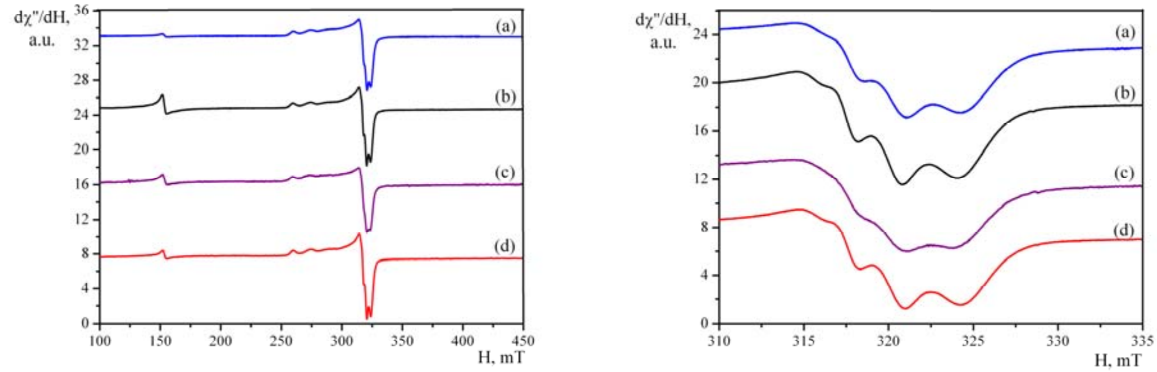

Fig. 2. The room temperature EPR spectra of the LTB:Cu (a, b) and KLTB:Cu (c, d) glasses, containing 0.4 mol.% (b, d) and 1.6 mol.% (a, c) of the CuO compound. Left side – complete EPR spectra, right side – central part of the EPR spectra.

As it can be seen from Fig. 2 the EPR spectra are virtually identical for Cu^{2+} centres in both LTB and KLTB glass matrices and consist of a pronounced band centred near $g = 2.34$ with weakly-resolved four-component structure and a relatively shallow quadruplet, centred about $g = 2.06$. Four weakly-resolved components are related to the HF structure, caused by nuclei of the ^{63}Cu and ^{65}Cu isotopes (natural abundance – 69.1 % of ^{63}Cu and 30.9 % of ^{65}Cu), which possess the same nuclear spin (I = 3/2) and similar values of nuclear magnetic moments (nuclear magnetic moment of ^{65}Cu is only 7.1 % higher than that of ^{63}Cu).

According to (Padlyak B. *et al.*, 2010) the observed Cu^{2+} EPR spectra in LTB:Cu and KLTB:Cu glasses can be described by the spin Hamiltonian of axial symmetry in the following form:

$$\hat{H} = g_{\|}\beta H_z \hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x + H_y\hat{S}_y) + \\ + A_{\|}\hat{S}_z\hat{I}_z + A_{\perp}(\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y) \qquad (1)$$

with parameters, which are determined at T = 300 K and presented in Table 3.

Table 3. The parameters of EPR spectra of the Cu^{2+} centres in tetraborate glasses

Glass composition	CuO amount (mol.%)	$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$ (mT)	$A_{\perp}$ (mT)	$\Delta H_{pp}^{\|\|}$ (mT)	$\Delta H_{pp}^{\perp}$ (mT)
$Li_2B_4O_7$:Cu	0.4	2.31 ± 0.05	2.07 ± 0.05	14.30 ± 0.05	2.61 ± 0.05	5.14 ± 0.05	1.85 ± 0.05
	1.6	2.30 ± 0.05	2.07 ± 0.05	14.45 ± 0.05	2.69 ± 0.05	5.38 ± 0.05	2.07 ± 0.05
$KLiB_4O_7$:Cu	0.4	2.31 ± 0.05	2.07 ± 0.05	15.34 ± 0.05	2.60 ± 0.05	5.38 ± 0.05	1.82 ± 0.05
	1.6	2.31 ± 0.05	2.07 ± 0.05	15.64 ± 0.05	2.60 ± 0.05	5.60 ± 0.05	1.97 ± 0.05

As we can see from Table 3, the EPR linewidth of the Cu^{2+} centres experiences homogeneous broadening with the increase of impurity concentration.

The observed $g_{\|}$ and $g_{\perp}$ values are practically independent of the basic glass composition and Cu concentration and are characteristic for $3d^9$ Jahn-Teller ions coordinated by six O^{2-} ligands that form an oxygen octahedron, elongated along the z axis. Some differences in hyperfine constants for Cu^{2+} centres in the LTB and KLTB glass network can be related to slight differences in the local environments of their second coordination sphere. According to (Witkowska A., Padlyak B. & Rybicki J., 2008), local environments in oxide glasses are similar in structure to the local environments in corresponding crystals. Thus, the Cu^{2+} impurity centres are most likely incorporated into the Li (K) cationic sites of LTB and KLTB glass network with coordination number to the oxygen $N = 6$ as in the corresponding teraborate crystals (Krogh-Moe J., 1968; Ono Y., Nakaya M., Kajitani T., Sugawara T., Watanabe N., Shiraishi H. & Komatsu R., 2000).

CONCLUSIONS

Based on the EPR spectra analysis of the Mn^{2+}, Cu^{2+} and Fe^{3+} impurity centres, registered in the $Li_2B_4O_7$ and $KLiB_4O_7$ glasses, doped with Mn and Cu in different concentration it was shown the following:

1. The manganese and copper impurities are incorporated into the LTB and KLTB glass network as paramagnetic Mn^{2+} ($3d^5$, $^6S_{5/2}$) and Cu^{2+} ($3d^9$, $^2D_{5/2}$) ions.
2. The Mn^{2+} ions are incorporated into the octahedral and tetrahedral sites of the tetraborate glass network as isolated centres and small exchange-coupled clusters for low and high Mn concentration, whereas the Cu^{2+} ions are incorporated into the octahedral sites of the glass structure as isolated centres, exclusively for low and high Cu concentration.
3. The isotropic Mn^{2+} centres in the LTB and KLTB glasses are characterized by EPR spectra, which are typical for other glassy compounds. Parameters of the Mn^{2+} EPR spectra for LTB:Mn and KLTB:Mn glasses, containing 0.4 and 1.6 mol.% of the MnO_2 were determined at T = 300 K. The obtained g_{iso} and A_{iso} values of the Mn^{2+} centres practically are independent of the basic glass composition and MnO_2 amount.
4. The Cu^{2+} EPR spectra in the LTB:Cu and KLTB:Cu glasses also are typical for disordered, in particularly glassy, compounds and are characterized by the axially-symmetric g-factor and hyperfine constant values. The spin Hamiltonian parameters of the Cu^{2+} centres for LTB:Cu and KLTB:Cu glasses, containing 0.4 and 1.6 mol.% of the CuO were determined at T = 300 K. The obtained g-factor values for Cu^{2+} centres are independent of the basic glass composition and CuO amount. Some differences in values of hyperfine constants for Cu^{2+} centres in the LTB:Cu and KLTB:Cu glasses can be related to slight differences in their local environments.
5. The increase of the dopant concentration leads to homogeneous broadening of EPR lines of the Mn^{2+}, Cu^{2+} and Fe^{3+} impurity centres, caused by the magnetic dipole-dipole interaction. The increasing of linewidth of the Fe^{3+} signal with increasing of the MnO_2 and CuO amounts allows concluding that the doping compounds are the main source of the iron non-controlled impurity in the investigated tetraborate glasses.

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REFERENCES

Brodbeck C. M. & Bukrey R. R. (1981). Model calculations for the coordination of Fe^{3+} and Mn^{2+} ions in oxide glasses. *Phys. Rev. B.* **25**, 2334-2342.

Burzo E. & Ardelean I. (1978). EPR study of Fe^{3+} ions in lead borate glasses. *Phys. Status Solidi B.* **87**, K137-K140.

Can N., Karali T., Townsend P. D. & Vildiz D. F. (2006). TL and EPR studies of Cu, Ag and P doped $Li_2B_4O_7$ phosphor. *J. Phys. D, Appl. Phys.* **39**, 2038.

Castner T., Newell G. S., Holton W. C. & Slichter C. P.(1960) Note on the paramagnetic resonance of iron in glass. *J. Chem. Phys.* **32**, 668-673

Griscom D. L. (1980). Electron spin resonance in glasses. *J. Non-Cryst. Solids.* **40**, 211-272.

Ignatovych M., Holovey V., Watterich A., Vidóczy T., Baranyai P., Kelemen A., Ogenko V. & Chuiko O. (2003). UV and electron radiation-induced luminescence of Cu- and Eu-doped lithium tetraborates. *Radiat. Phys. Chem.* **67**, 587-591. (2003).

Ignatovych M., Holovey V., Vidóczy T., Baranyai P., Keleman A., Laguta V. & Chujko O. (2005). Spectroscopy of the Cu- and Ag-doped single crystal and glassy tetraborate: luminescence, optical absorption and ESR studies. *Funct. Mater.* **12**, 313-317.

Ignatovych M., Holovey V., Vidóczy T., Baranyai P. & Kelemen A. (2007). Spectral study on manganese- and silver-doped lithium tetraborate phosphors. *Radiat. Phys. Chem.* **76**, 1527-1530.

Krogh-Moe J. (1968). Refinement of the crystal structure of lithium diborate $Li_2O.2B_2O_3$. *Acta Cryst. B.* **24**, 179-181.

Ono Y., Nakaya M., Kajitani T., Sugawara T., Watanabe N., Shiraishi H. & Komatsu R. (2000) Lithium potassium borate and lithium rubidium borate: new non-linear optical crystals. *Acta Cryst.* C **56**, 1413-1415

Padlyak B.V. & Gutsze A. (1998). EPR study of the impurity paramagnetic centres in (CaO-Ga_2O_3-GeO_2) glasses. *Appl. Magn. Reson.* **14**, 59-68.

Padlyak B. V., Wojtowicz W., Adamiv V. T., Burak Ya.V. & Teslyuk I. M. (2010). EPR spectroscopy of the Mn^{2+} and Cu^{2+} centres in lithium and potassium-lithium tetraborate glasses. *Acta Phys. Pol. A.* **117**, 122-125.

Podgórska D., Kaczmarek S. M., Drozdowski W., Wabia M., Kwasny M., Warchol S. & Rizak V. M. (2004). Recharging processes of Mn ions in $Li_2B_4O_7$:Mn single crystal and glass samples under the influence of γ-irradiation and annealing. *Mol. Phys. Rep.* **39**, 199-222.

Prokic M. (2002). Dosimetric characteristics of $Li_2B_4O_7$:Cu, Ag, P solid TL detectors. *Radiat. Prot. Dosim.,* **100**, 265-268.

Santiago M., Lester M., Caselli E. & Lavat A. (1998). Thermoluminescence of sodium borate compounds containing copper. *J. Mater. Sci. Lett.* **17**, 1293-1296.

Senguttuvan N., Ishii M., Shimoyama M., Kobayashi M., Tsutsui N., Nikl M., Dusek M., Shimizu H. M., Oku T., Adachi T., Sakai K. & Suzuki J. (2002), Crystal growth and luminescence properties of $Li_2B_4O_7$ single crystals doped with Ce, In, Ni, Cu and Ti ions. *Nucl. Instrum. Methods Phys. Res. A.* **486**, 264-267.

Witkowska A., Padlyak B. & Rybicki J. (2008). An EXAFS study of the local structure of rare-earth luminescence centres in the $3CaO$-Ga_2O_3-$3GeO_2$ glass, *Opt. Mater.* **30**, 699-702.

Zadneprowski B. I., Eremin N. E. & Paskhalov A. A. (2005). New inorganic scintillators on the basis of LBO glass for neutron registration. *Funct. Mater.* **12**, 261-268.