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THERMAL NEUTRON IRRADIATION EFFECT OF LITHIUM BORATE GLASSES

Tetsuaki NISHIDA* and Yoshimasa TAKASHIMA
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812

Nuclear reactions of $^{10}B(n,\alpha)^{7}Li$ and $^{6}Li(n,\alpha)^{3}H$ result in an increase in the Mössbauer absorption area of Fe^{2+}, and the irradiation effect caused by the latter reaction proves to be remarkable when the alkali oxide (Li_2O) content is low. This is ascribed to the open structure of the borate glasses where BO_3 triangles are superior in numbers to BO_4 tetrahedra.

Mössbauer study of several kinds of glasses irradiated with thermal neutrons has already been reported on borate[1,2] and borosilicate[3] glasses, where an increase in s-electron density at iron nucleus[1,3] or a reduction of Fe^{3+} to Fe^{2+} ion[2] has been observed as a result of $^{10}B(n,\alpha)^{7}Li$ nuclear reaction. These electronical changes on the iron (Fe^{3+}) caused by the irradiation have been ascribed to the elastic and inelastic collision of several ions or atoms in those glasses with the charged particles (α and ^{7}Li) produced in the nuclear reaction. In a case of potassium borate glasses[2] containing a small amount of $^{57}Fe_2O_3$, the number of Fe^{3+} ions reduced to Fe^{2+} per one α or ^{7}Li particle was estimated by utilizing the Mössbauer absorption area. A continuous increase in the number of Fe^{2+} ions produced by the $^{10}B(n,\alpha)^{7}Li$ reaction has also been observed in the borate glasses[2] when the alkali oxide (K_2O) content exceeds 20 mol%. This is ascribed to the presence of nonbridging oxygen (NBO, $-O^{-}$), of which energy level is considered to be higher than that of bridging oxygen. Nuclear reaction of $^{6}Li(n,\alpha)^{3}H$ has also been paid much attention in connection with the chemical effects in the blanket materials used in a fusion reactor.[4] The present study was carried out to elucidate the additional irradiation effect brought about by $^{6}Li(n,\alpha)^{3}H$ reaction in borate glasses in which lithium ion is chosen as a network modifier instead of potassium ion described above.

Transparent and almost colorless lithium borate glasses containing a small amount of iron were prepared by quenching the individual melts composed of Li_2CO_3, H_3BO_3, and $^{57}Fe_2O_3$ (^{57}Fe = 90.24%) of guaranteed reagent grade. Each batch in a platinum crucible was fused at 1000 °C for 3 h in an electric muffle furnace. The composition of the glass sample is denoted as $xLi_2O\cdot(100-x)B_2O_3\cdot0.33Fe_2O_3$, where x is changed from 15 to 40 at 5 intervals. Thermal neutron irradiation was performed at the Research Reactor in the Atomic Energy Institute of Rikkyo University for 3 min and 30 min at the ambient temperature. The thermal neutron flux and the γ-ray dose rate are 5 X 10^{11} n cm^{-2} s^{-1} and 1 X 10^6 R h^{-1}, respectively. Absorption Mössbauer spectra were measured by the constant acceleration method at room temperature. Cobalt-57 diffused into a palladium foil was used as the Mössbauer source. Metallic iron foil enriched with ^{57}Fe was used as a reference for isomer shift and also for calibrating the velocity of the spectrometer. All the Mössbauer spectra were analyzed into Lorentzians by using a least-squares method.

Mössbauer spectrum for all the unirradiated lithium borate glasses prepared in the present study consists of two kinds of quadrupole doublets due to Fe^{2+} and Fe^{3+}. It is very rare case that the spectrum for the unirradiated borate glasses shows an absorption due to Fe^{2+}, and all the unirradiated borate glasses studied so far show a quadrupole doublet due to Fe^{3+} ions irrespective of the iron content of the glasses.[1,2,5-7] This may be due to the increasing oxidizing atmosphere of the glass matrix when the network-forming atom is changed from more electronegative element to less electronegative one, e.g., in the order of P (phosphate[8,9]), B (borate[1,2,5-7]), and Si (borosilicate[3]). This will be also the case for the network modifying cation, and the oxidizing atmosphere will increase in the order of Li^+, Na^+, and K^+. It is also known that an increase in the basicity of glass, which is inversely correlated with the single bond strength of the constituent cations,[10] results in an increased oxidation state of metal ions in the glasses. The present result is also consistent with this empirical rule. Mössbauer parameters for the unirradiated lithium borate glasses are summarized in Table 1, from which it is obvious that all the iron atoms are present at tetrahedral environments, as a network former, as in the case of potassium borate glasses,[1,2,]

Table 1. Mössbauer parameters for lithium borate glasses

Composition	Species	δ [a] / mm s^{-1}	Δ [b] / mm s^{-1}	Γ [c] / mm s^{-1}	A [d] / %
$15Li_2O\cdot85B_2O_3\cdot0.33Fe_2O_3$	Fe^{3+}	0.38	1.25	1.03	82.8
	Fe^{2+}	0.93	2.88	0.97	17.2
$20Li_2O\cdot80B_2O_3\cdot0.33Fe_2O_3$	Fe^{3+}	0.36	1.30	1.13	84.2
	Fe^{2+}	0.98	2.58	0.93	15.8
$25Li_2O\cdot75B_2O_3\cdot0.33Fe_2O_3$	Fe^{3+}	0.35	1.14	1.16	81.2
	Fe^{2+}	0.93	2.54	0.89	18.8
$30Li_2O\cdot70B_2O_3\cdot0.33Fe_2O_3$	Fe^{3+}	0.32	1.23	1.22	84.6
	Fe^{2+}	1.03	2.35	0.80	15.4
$35Li_2O\cdot65B_2O_3\cdot0.33Fe_2O_3$	Fe^{3+}	0.30	1.12	1.18	83.4
	Fe^{2+}	0.99	2.24	0.85	16.6
$40Li_2O\cdot60B_2O_3\cdot0.33Fe_2O_3$	Fe^{3+}	0.30	1.15	1.13	82.6
	Fe^{2+}	1.02	2.25	0.93	17.4

a) Isomer shift. b) Quadrupole splitting. c) Linewidth. d) Absorption area.

5-7) because most isomer shifts with respect to metallic iron are smaller than 1.0 and 0.4 mm s^{-1} which can be criteria for tetrahedral Fe^{2+} and Fe^{3+} species, respectively. (Lithium borate glass denoted by $10Li_2O\cdot 90B_2O_3\cdot 0.33Fe_2O_3$ is not studied in the present study because a completely glassy sample could not be obtained.)

Mössbauer parameters for the irradiated lithium borate glasses are almost consistent with those for the unirradiated glasses shown in Table 1, except for the absorption area which is also shown in Fig. 1. The absorption area of Fe^{2+} in the thermal neutron irradiated potassium borate glasses[2] containing 0.33 mol% of Fe_2O_3 is also shown for comparison. It is seen from Fig. 1 that the absorption area of Fe^{2+} increases by the thermal neutron irradiations of 3 min (Fig. 1b) and 30 min (Fig. 1c). Figure 1 shows a remarkable increase in the Fe^{2+} fraction when the lithium oxide content is low. This is a surprizing result, because γ-ray or thermal neutron irradiation experiments performed so far result in a constant absorption area when the alkali oxide content is low,[2,6] as is also shown in Fig. 1d. It is obvious from Figs. 1c and 1d that the substitution of Li^+ for K^+ in borate glasses results in an increase in the Fe^{2+} fraction when irradiated with thermal neutrons. This is ascribed to the increased irradiation effect caused by the $^6Li(n,\alpha)^3H$ reaction in a case of lithium borate glasses. (Contribution of the in-pile γ-rays in the thermal neutron irradiation effect has already been estimated only to be 10-15%,[2] and therefore the irradiation effect caused by γ-rays can be neglected in the present discussion.) Similar increase in the Fe^{2+} fraction produced by $^6Li(n,\alpha)^3H$ reaction is also observed by Akashi et al.[11,12] in a case of lithium tris (oxalato) ferrate(III) crystal.

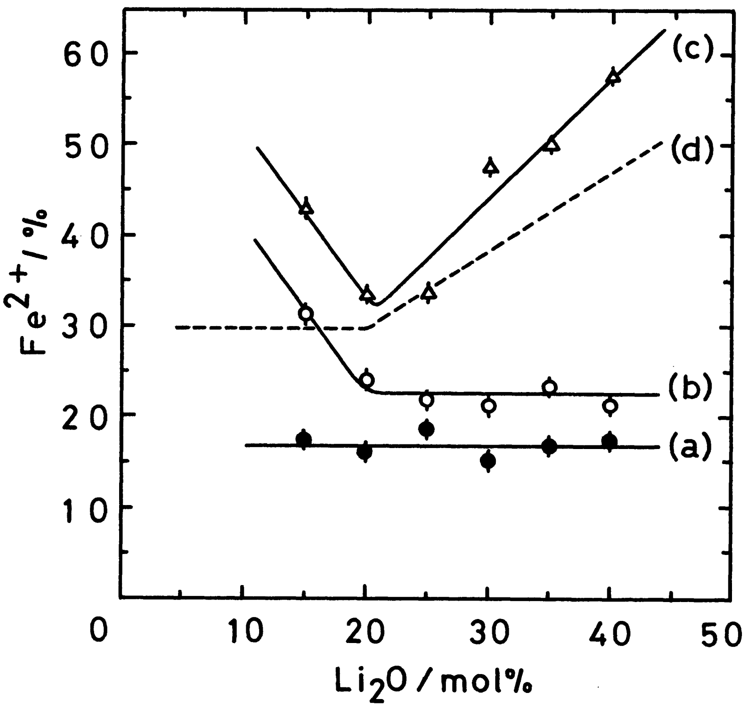

Fig. 1. Mössbauer absorption area of Fe^{2+} in lithium borate glasses. (a): unirrad., (b): 3 min-irrad., (c): 30 min-irrad. The broken line (d) refers to the result of 30 min-irradiated potassium borate glasses.[2]

The larger fraction of Fe^{2+} in the low alkali oxide content region (x = 15) may be due to the open structure of the borate glasses, in which BO_3 triangles are superior in numbers to BO_4 tetrahedra. It is well known that some physical properties of borate glasses such as density and refractive index show maxima when the alkali oxide cencentration is about 20 mol% (i.e., boron anomaly). The present result seems to be inversely correlated with the abnormal change in the density, and the chemical effect brought about by $^{6}Li(n,\alpha)^{3}H$ reaction will be well reflected when the glass-forming atoms or ions are loosely packed, probably because lithium ion is present at an interstitial site as a network modifier. This is also the case for the lithium borate glasses with higher alkali oxide contents, i.e., the increasing Fe^{2+} fraction in the 30 min-irradiated lithium borate glasses (Fig. 1c) observed with increasing alkali oxide content, when x is larger than 20, can be ascribed to the combined irradiation effects caused by $^{6}Li(n,\alpha)^{3}H$ and $^{10}B(n,\alpha)^{7}Li$ reaction. The latter reaction, as also described above, is already reported to result in an increased Fe^{2+} fraction when the fraction of NBO in BO_4 units increases.[1-3] The thermal neutron irradiation of lithium borate glasses is therefore concluded to reduce more Fe^{3+} ions to Fe^{2+} state than that of potassium borate glasses, in the higher alkali oxide region, because the $^{6}Li(n,\alpha)^{3}H$ reaction brings about more significant irradiation effect when the structure of the borate glasses becomes open, i.e., when many NBO atoms are present. Many electrons will be therefore transferred from the neighboring oxygen atoms to Fe^{3+} ions as a result of the $^{6}Li(n,\alpha)^{3}H$ reaction in lithium borate glasses.

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