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Mössbauer Spectroscopic Study of γ-Ray Irradiated Potassium Borate Glasses

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Potassium borate glasses denoted by the formula $x\mathrm{K_2O} \cdot (100 - x)\mathrm{B_2O_3} \cdot 7\mathrm{Fe_2O_3}$ were irradiated with ^{60}Co-γ-rays at room temperature. Mössbauer parameters for the irradiated glasses containing alkali equal to or higher than 20 mole% showed that the s-electron density at the iron nucleus increased without any change of the steric configuration of oxygen atoms around the iron nucleus. The increase of s-electron density was ascribed to electron transfer from the nonbridging oxygen to the iron nucleus. The presence of the nonbridging oxygen was also confirmed by the irradiation effect of the borate glass ($x = 30$) prepared using the enriched isotope of $^{57}\mathrm{Fe_2O_3}$. Mössbauer parameters for the irradiated glass suggest that the newly observed $\mathrm{Fe^{2+}}$ ions are in tetrahedral symmetry.

Introduction

The formation of nonbridging oxygen (NBO) in the borate glasses is suggested to start from alkali concentrations higher than about 20 mole% (*1–3*). Assabghy *et al.* (*1*) showed the presence of NBO vacancies in γ-ray irradiated borate glasses using the ESR technique. Mössbauer spectroscopic study was also carried out by Raman *et al.* (*2*) and the authors (*3*), where the decrease of Mössbauer parameters was observed with increasing alkali concentration in the glasses. The decrease was ascribed to the presence of NBO atoms in the glasses. The present study was performed to confirm the presence of NBO in the borate glasses, on the basis of the idea that the NBO is rather sensitive to γ-rays compared to the bridging oxygen.

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Experimental

Potassium borate glasses containing small amounts of iron were prepared by melting mixtures of weighed quantities of $\mathrm{K_2CO_3}$, $\mathrm{H_3BO_3}$, and $\mathrm{Fe_2O_3}$ of guaranteed reagent grade. Each mixture was melted using a platinum crucible at 1000°C for 3 hr in an electric furnace and quenched quickly with cold water in a beaker. The borate glasses are denoted by the formula $x\mathrm{K_2O} \cdot (100 - x)\mathrm{B_2O_3} \cdot 7\mathrm{Fe_2O_3}$, where the x value was changed from 15 to 35 mole%.

The ^{60}Co-γ-ray irradiation of the glasses was carried out at room temperature in the irradiation facility of the Japan Atomic Energy Research Institute in Tokai.

The absorption Mössbauer spectra were

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measured by the constant acceleration method at room temperature, with the source of cobalt-57 (5 mCi) diffused into palladium foil. The velocity of the spectrometer was calibrated using a pure iron foil, which was also used as a reference for the isomer shift. All spectra were fitted to Lorenzian lineshapes using a computer program.

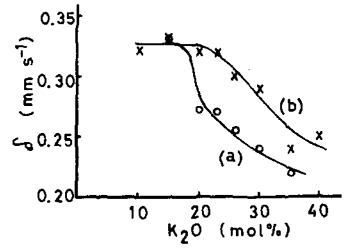

FIG. 1. The decrease of isomer shift as a function of the alkali content of the borate glasses: (a) after γ-ray irradiation (present work); (b) before irradiation (cited from Ref. (3)).

Results and Discussion

The potassium borate glasses were transparent dark brown in every case. The homogeneity of the glasses was confirmed by use of X-ray diffractometry as given in a previous paper (3). The Mössbauer spectrum of the γ-irradiated (3×10^8 R) glasses consisted of one doublet which is characteristic of Fe^{3+} with Td symmetry. These results were summarized in Table I. The isomer shift and quadrupole splitting values decreased with alkali content of the glasses. The decrease of quadrupole splitting value was just the same as the decrease in the nonirradiated glasses (3); however, the isomer shift value decreased more distinctly in the irradiated glasses (Fig. 1). The decrease of quadrupole splitting value shows the increase of symmetry around the Fe^{3+} ions in the glasses. The results on the quadrupole splitting therefore mean that the steric configuration around the Fe^{3+} ions is still retained after the γ-ray irradiation. On the other hand, the decrease of the isomer shift means increase of *s*-electron density at the iron nucleus, and therefore the irradiation-induced decrease of the isomer shift means electron transfer from oxygen ions to the Fe^{3+} ions. It seems that the number of electrons transferred is not great because no reduced species were observed in the Mössbauer spectrum. It is interesting to note that the irradiation-induced decrease of isomer shift is limited to the glass for which the alkali content is equal to, or higher, than 20 mole%. It was suggested by the authors that the formation of NBO starts from this alkali concentration (3). It is not inconsistent with the ESR results by Assabghy *et al.* (1).

TABLE I

MÖSSBAUER PARAMETERS FOR THE γ-RAY IRRADIATED BORATE GLASSES (mm sec^{-1})

x	δ	Δ	Γ
15	0.33	1.09	0.64
20	0.27	1.08	0.67
23	0.27	0.97	0.64
26	0.25	0.97	0.73
30	0.24	0.90	0.56
35	0.22	0.87	0.51

The extra oxygens in the oxide glasses, i.e., NBO atoms, can be used for bonding with atoms other than network formers (e.g., B, P and Si). It can be considered that Fe^{3+} ions are surrounded by NBO atom(s) in the borate glasses, and that the chemical bonds between boron and NBO atoms are easily disrupted as compared with those between bridging oxygen and boron atoms. Some of the valence electrons which are used to bind boron and NBO atoms will therefore be trapped by the Fe^{3+} ions during the irradiation. The number of electrons trapped by Fe^{3+} ions will increase with the γ-ray dose, but the decrease of isomer shift is not considered to be infinite because the Fe^{3+} ions are in a high-spin state in the borate glasses. Potassium borate glass which contains 0.16 mole% of $^{57}Fe_2O_3$ was prepared (x = 30) and irradiated to clarify the electron transfer to the Fe^{3+} ions, because it was expected that the number of Fe^{3+} ions was much higher than that of the trapped electrons. This borate glass was prepared so that the total $^{57}Fe^{3+}$ content in the glass becomes the same as the content in the glasses prepared using natural iron oxide. Total γ-ray dose was also identical with that of other glasses (3×10^8 R). Mössbauer parameters for the nonirradiated glass were the same as those for the corresponding glass, except that the linewidth increased ca. 50%. The Mössbauer spectrum for the γ-ray irradiated glass is shown in Fig. 2. The spectrum consists of two doublets, for which the Mössbauer parameters are characteristic of high-spin Fe^{3+} and Fe^{2+} species. Isomer shift and quadrupole splitting values for absorption I are 0.35 and 0.73 mm sec^{-1}, respectively. This isomer shift value of 0.88 mm sec^{-1} shows that the irradiation-induced Fe^{2+} species are also in tetrahedral symmetry. The absorption area for Fe^{2+} was calculated to be 58% by computer analysis on the basis of the assumption that the recoilless fraction for Fe^{2+} is the same as the fraction for Fe^{3+} in the glass

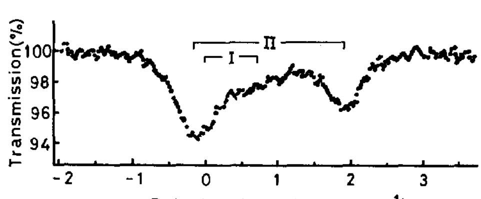

FIG. 2. Mössbauer spectrum of the γ-ray irradiated potassium borate glass (x = 30) containing 0.16 mole% of $^{57}Fe_2O_3$.

structure. The quantity of Fe^{2+} ions produced by γ-rays with the total dose of 3×10^8 R is therefore estimated to be 0.20 mole%, since the enrichment of iron-57 in the reagent, $^{57}Fe_2O_3$, is 92.36%. The number of electrons trapped by Fe^{3+} ions is also 0.20% ($e^- = 1.2 \times 10^{21}$ $mole^{-1}$).

The absorptions due to both Fe^{2+} and Fe^{3+} ions have been observed in the Mössbauer spectrum of oxide glasses (*4–6*) other than borate glasses. On the other hand, only Fe^{3+} ions have been observed in the borate glasses (*2, 3*). This can be explained by the number of valence electrons of the boron atom, i.e., there are only three electrons in the sp^3 hybrid orbital, and therefore the boron atom will attract electrons to form BO_4 tetrahedron. In the light of this reason, it is very significant that an increase of s-electron density at the iron nucleus was observed in the borate glasses prepared using natural Fe_2O_3. It is also very interesting that Fe^{3+} ions were reduced to Fe^{2+} by the irradiation of the borate glass with low concentration of iron, which is essentially acidic in nature. This reduction also verifies that the NBO atoms are present in the borate glass when the alkali content is equal to, or higher than, 20 mole%.

Acknowledgments

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