December, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 3735—3738 (1981) 3735

Mössbauer Spectroscopic Study of Potassium Borosilicate Glasses at Low Temperatures

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(Received January 26, 1981)

The Mössbauer technique at the liquid nitrogen temperature (78 K) was applied to the estimation of non-bridging oxygens in FeO_4, BO_4, and SiO_4 units in potassium borosilicate glasses. Mössbauer spectra consist of a quadrupole doublet and a hyperfine structure due to Fe^{3+} ions with tetrahedral symmetry. The hyperfine structure is attributed to a relaxation effect because magnetic susceptibility measurements revealed the glasses to be paramagnetic in the temperature range 78—295 K. A linear decrease in the absorption area and a similar decrease in the internal magnetic field for the hyperfine structure were observed with an increase in the alkali content of glasses. The decrease is ascribed to a formation of non-bridging oxygen at the site adjacent to iron, because the mean life-time of the internal magnetic field produced by 3d-electrons of iron is considered to decrease with increasing thermal vibration of the iron and neighboring oxygens. Fractions of non-bridging oxygens obtained from the reduction rate of the absorption area of hyperfine structure are in good agreement with earlier results for borate glasses with the same K_2O/B_2O_3 ratios, in the alkali region of 8—20 mol% where the borosilicate glasses are essentially considered to be borate glasses diluted with SiO_2.

NMR studies by Yun and Bray$^{1)}$ reported on each fraction of BO_3 and BO_4 units in various borate or borosilicate glasses, where the fraction of BO_4 unit proved to increase linearly with the alkali content of glasses in the low alkali region. Mössbauer technique was also applied to studying the structure of borate glasses,$^{2-7)}$ and a formation of non-bridging oxygen (NBO) was suggested to start at an alkali content of 20 mol%. The fraction of NBO in the oxygens constituting BO_4 or FeO_4 units was also estimated from a Mössbauer study of γ-ray irradiated borate glasses,$^{6)}$ and from a study at low temperatures.$^{7)}$ A Mössbauer study of potassium borosilicate glasses$^{8)}$ suggested the formation of NBO to start at an alkali content of 8 mol% in the case of borosilicate glasses with an SiO_2/B_2O_3 ratio of 2.0. It was also considered that the fraction of NBO in borosilicate glasses is increased as a result of the substitution of B_2O_3 for SiO_2.

The present study was performed to estimate the fraction of NBO in potassium borosilicate glasses by using the Mössbauer technique at low temperatures.

Experimental

Potassium borosilicate glasses denoted by the formula $x\,K_2O\cdot(100-x)(B_2O_3,\ SiO_2)\cdot 0.33\,Fe_2O_3$ were prepared by melting mixtures of weighed quantities of K_2CO_3, H_3BO_3, SiO_2, and Fe_2O_3 of guaranteed reagent grade. As for the iron(III) oxide, an enriched isotopic species $^{57}Fe_2O_3$ ($^{57}Fe=90.24\%$) was used for the preparation. The value of x was changed from 12 to 40, and the molar ratio of SiO_2 to B_2O_3 was so chosen as to be 2.0. Each mixture in a platinum crucible was melted at 1300 °C for 3 h in an electric muffle furnace. The melt was sometimes stirred to be made homogeneous, and was quenched by steeping the platinum crucible into cold water in a beaker. Amorphous structure of almost colorless and transparent glasses was confirmed by X-ray diffractometry. All the glass samples were preserved in a desiccator to protect them from the atmospheric moisture.

Mössbauer measurements were performed by the constant acceleration method at room (295 K), Dry Ice (196 K), and liquid nitrogen (78 K) temperatures. Cobalt-57 (5 mCi) diffused into a palladium foil was used as the source, and the velocity of the spectrometer was calibrated using a pure iron foil enriched with iron-57. The iron foil was used as a reference for isomer shift values. All the spectra were fitted to Lorenzian line shape by computer calculations.

Results and Discussion

Mössbauer spectra for the potassium borosilicate glass with an alkali content of 12 mol% are shown in Fig. 1. All the Mössbauer spectra at room and Dry Ice temperatures consist of a quadrupole doublet (qd) due to the Fe^{3+} ions with tetrahedral symmetry,$^{2-12)}$ together with a marked wing shape of base line. Isomer shift values of the quadrupole doublet are consistent with the corresponding values of the borosilicate glasses containing 7 mol% Fe_2O_3.$^{8)}$ Mössbauer spectra for the borosilicate glasses containing 0.33 mol% Fe_2O_3 can, therefore, be analyzed in the same way as for the borosilicate glasses containing 7 mol% Fe_2O_3, although each of the spectra has a wing shape of base line. This is also the case for the Mössbauer spectra at the liquid nitrogen temperature, *i.e.*, the isomer shift values of the quadrupole doublet are well consistent with the corresponding values of the borosilicate glasses containing 7 mol% Fe_2O_3.

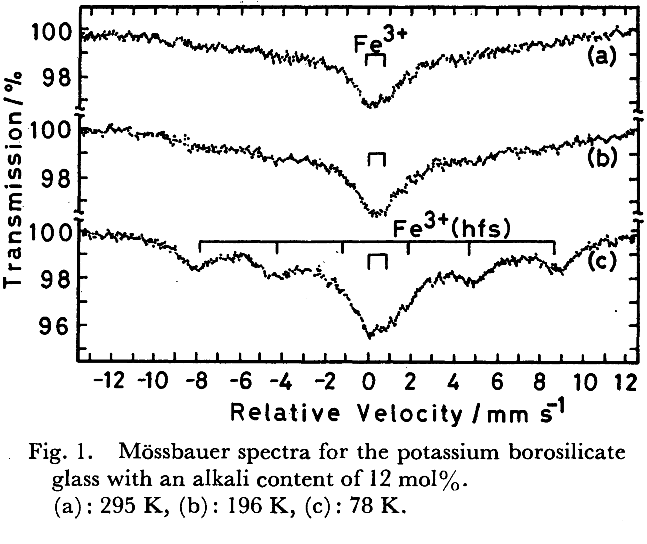

Fig. 1. Mössbauer spectra for the potassium borosilicate glass with an alkali content of 12 mol%.
(a): 295 K, (b): 196 K, (c): 78 K.

Mössbauer spectra at the liquid nitrogen temperature are, therefore, analyzed into a quadrupole doublet and six absorptions of hyperfine structure (hfs). The hfs suggests that the ^{57}Fe nuclei are in the magnetic field and that the mean lifetime of the internal magnetic field is at least of the order of nuclear Larmor precession time. Magnetic susceptibility measurements were then performed to confirm the hfs to be due to a paramagnetic relaxation effect and not due to a magnetic transition or magnetic impurities in the glasses. The data is shown in Fig. 2, which proves the borosilicate glasses to be paramagnetic in the temperature range 78—295 K where the hfs and/or the marked wing shape of base line were observed.

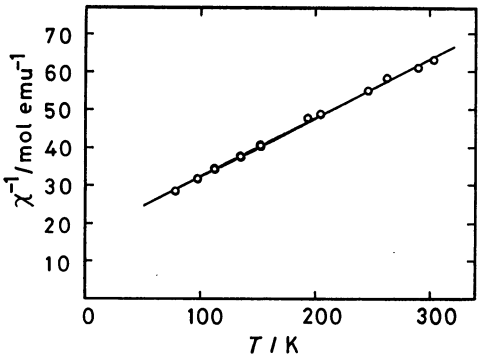

Fig. 2. Magnetic susceptibility measurements of the potassium borosilicate glass with an alkali content of 12 mol%.

TABLE 1. MÖSSBAUER PARAMETERS FOR THE POTASSIUM BOROSILICATE GLASSES AT 78 K

$X^{a)}$ mol%	Species	$\delta^{b)}$ mm s^{-1}	$\Delta^{c)}$ mm s^{-1}	$\Gamma^{d)}$ mm s^{-1}	$A^{e)}$ %
12	Fe^{3+}(qd)	0.41	0.89	0.73	32.1
12	Fe^{3+}(hfs)	0.39	−0.14	0.77	67.9
15	Fe^{3+}(qd)	0.38	0.61	0.70	37.4
15	Fe^{3+}(hfs)	0.37	−0.07	0.67	62.6
20	Fe^{3+}(qd)	0.36	0.75	1.03	37.9
20	Fe^{3+}(hfs)	0.33	−0.12	0.96	62.1
25	Fe^{3+}(qd)	0.30	0.68	0.85	39.4
25	Fe^{3+}(hfs)	0.35	−0.07	0.57	60.6
30	Fe^{3+}(qd)	0.30	0.65	0.78	42.0
30	Fe^{3+}(hfs)	0.32	−0.03	0.69	58.0
40	Fe^{3+}(qd)	0.32	0.80	0.86	43.3
40	Fe^{3+}(hfs)	0.34	−0.06	0.64	56.7

a) Alkali content. b) Isomer shift. c) Quadrupole splitting. d) Line width (FWHM). e) Absorption area.

The Mössbauer parameters obtained at the liquid nitrogen temperature are summarized in Table 1. The experimental error including the one from computer calculation is estimated to be ±0.02 mm s^{-1} or more for the isomer shift, since the spectrum is less sharp than the one for the corresponding borosilicate glass containing 7 mol% Fe_2O_3.[8] In the latter case, the error was estimated to be ±0.01 mm s^{-1}, and the spectrum consists only of a quadrupole doublet free from the relaxation effect. Errors are also estimated to be ±0.02 mm s^{-1} for the quadrupole splitting and the line width and ±0.1% for the absorption area. All the isomer shift values for the Fe^{3+} ions with tetrahedral symmetry are increased because of the decreased second-order Doppler effect at lower temperatures. Table 1 also demonstrates that isomer shift values decrease with increasing alkali content of the glasses, as in the case of borosilicate glasses containing 7 mol% Fe_2O_3[8] measured at room temperature. A continuous decrease in isomer shift with increasing alkali content has already been attributed to a formation of NBO in borate[2—5,7] or borosilicate[8] glasses. The decrease in isomer shift indicates an increased s-electron density at iron nucleus as a result of the formation of NBO at the site adjacent to the iron. The increase in s-electron density can be explained by the increased overlap of the 4s-orbital of iron with the 2*p*-orbital of NBO, followed by the transfer of electron from the NBO to the iron. The electron transfer has also been confirmed by the reduction of Fe^{3+} to Fe^{2+} in borate glasses irradiated with γ-rays.[4,6] The increased s-electron density is also explained by the decreased screening effect of s-electrons by p-electrons, because more electrons (3/4 of which are considered to be p-electron) in the sp^3 hybrid orbital will be attracted to the NBO than to the bridging oxygens. The decrease in isomer shift in borosilicate glasses is thus attributed to a formation of NBO at sites adjacent to iron, boron, and silicon in FeO_4, BO_4, and SiO_4 units, respectively.

The quadrupole splitting values for the quadrupole doublet are also consistent with results for Fe^{3+} ions with tetrahedral symmetry in glasses.[2—12] The negative sign of the quadrupole splitting values for the hfs demonstrates that the direction of the electric field gradient tensor is parallel to the xy plane of the network structure. The very small quadrupole splitting values for the hfs suggest that the direction of the electric field gradient tensor is also the same as that of the internal magnetic field. The small quadrupole splitting may be observed probably because the direction of the internal magnetic field depends upon the relaxation time of 3d-electrons, and therefore upon the measuring temperature. It is, therefore, assumed that the magnitude of the quadrupole splitting for the hfs would become as large as the corresponding value for the quadrupole doublet, at much lower temperatures. All the line width (FWHM) values are also characteristic of the absorptions for irons in glasses,[2—12] and are a little increased because of a relaxation effect.

Figures 3 and 4 show changes of the absorption area and the internal magnetic field for the hfs, respectively. The internal magnetic field was obtained by comparing the distance between the outermost absorptions of the hfs with the corresponding distance of a pure iron foil with an internal magnetic field of 330 kOe at room temperature. It is obvious from Figs. 3 and 4 that there occurs a distinct change of glass structure at the alkali region of 16—18 mol%, because all the glasses were prepared so that the iron content should be equal to each other (0.33 mol%), and because all the spectra were measured at the same temperature (78 K). These results are consistent with the NMR results by Yun and Bray[1] that the borosilicate glasses are essentially

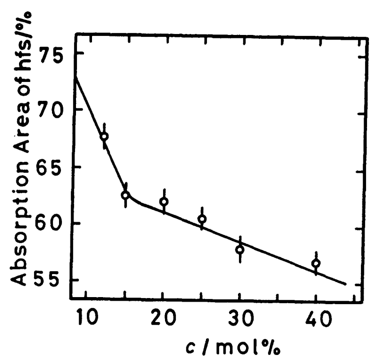

Fig. 3. Mössbauer absorption area of hyperfine structure (hfs) at 78 K plotted against the alkali content of potassium borosilicate glasses.

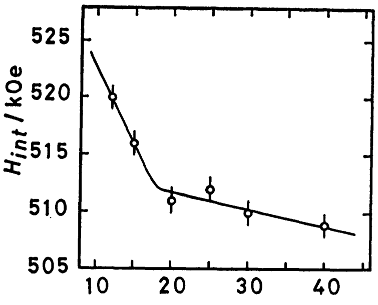

Fig. 4. Internal magnetic field for hyperfine structure (hfs) at 78 K plotted against the alkali content of potassium borosilicate glasses.

considered to be borate glasses diluted with SiO_2 in the alkali region lower than 18 mol%. The additional alkali oxide molecules will therefore be attracted to BO_3 units to form BO_4 units with and without NBO in the alkali region of 8—18 mol%. Formation of BO_4 unit with only bridging oxygens is assumed to occur in the alkali region lower than 8 mol%. In the alkali region higher than 18 mol%, the additional alkali oxide will also be attracted to SiO_4 units to form NBO. The decreasing absorption area of hfs (Fig. 3) can therefore be correlated with the fraction of NBO in FeO_4 units, and also with the fraction in BO_4 and SiO_4 units because all the irons are considered to be present at the substitutional site of boron or silicon. The decrease in the absorption area of hfs is well explained by taking account of the thermal vibration at a certain temperature, *e.g.*, 78 K. The thermal vibration of oxygen is considered to be more frequent in the case of NBO as compared with bridging oxygen, because the former is bonded with only one network former such as iron, boron, or silicon and the latter is bonded with two atoms of network formers.⁷⁾ It is, therefore, considered that the thermal vibration of iron is also more frequent in the case of the iron bonded with NBO. Therefore, the internal magnetic field produced by 3d-electrons of iron⁷⁾ is considered to be closely correlated with the fraction of NBO in FeO_4 units, because the mean lifetime of the internal magnetic field will be reduced with increasing thermal vibration, *i.e.*, with increasing NBO fraction. The reduction rate of the absorption area for the hfs, therefore, seems to be useful for the estimation of NBO fraction at the site adjacent to iron, because the paramagnetic hfs (relaxation spectrum) is observed as a result of the interaction of the Mössbauer nuclei (^{57}Fe) with the internal magnetic field produced by 3d-electrons of the irons.⁷⁾ Fractions of NBO at individual alkali concentrations are summarized in Table 2, where the absorption areas of the hfs at 8 and 10 mol% were obtained by extrapolation of the straight line shown in Fig. 3. The absorption area at the alkali content of 35 mol% was obtained by interpolation of the straight line of Fig. 3. Each of the NBO fractions was obtained by dividing the decreased absorption area by the absorption area at the alkali content of 8 mol% (*i.e.*, 73.0%) where the formation of NBO is considered to start.⁸⁾ All the fractions of NBO seem to be reasonable, because the values in the alkali region lower than 20 mol% are consistent, within the experimental error, with earlier results for potassium borate glasses⁶,⁷⁾ having the same K_2O/B_2O_3 ratios as in the borosilicate glasses. The borosilicate glasses are, therefore, considered to be borate glasses diluted with SiO_2 in the alkali region lower than 18 mol%, as described above. The present method seems to be very useful for the estimation of NBO in borate or borosilicate glasses. It is expected that the absorption area for the hfs increases with decreasing iron content of the glasses, and also with a decrease in the measuring temperature. The experimental error for the calculation of absorption area will be reduced with increasing hfs, because the spectral analysis of the innermost peaks is somewhat uncertain in the case of partially relaxed spectra. The fractions of NBO obtained in the present study, however, are considered to be reasonable because each of them was obtained from the relative absorption area of hfs and not from the absolute absorption area of hfs.

Table 2. Estimation of non-bridging oxygens in potassium borosilicate glasses

$X^{a)}$ / mol %	Absorption area of hfs/%	Fraction$^{b)}$ of NBO/%
8	73.0	0
10	70.2	3.8±1.9
15	63.0	13.7±1.9
20	61.2	16.1±1.9
25	59.8	18.1±2.0
30	58.6	19.7±2.0
35	57.3	21.5±2.0
40	56.0	23.3±2.0

a) Alkali content. b) Estimated from the decrease in the absorption area of hfs.

The authors are grateful to Dr. Shuji Emori of Saga University for his kind help in the magnetic susceptibility measurements of the glass samples. They are also grateful to Dr. Yusuke Nakayama of Ehime University for his kind suggestions in the computer analyses of the Mössbauer spectra. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 347036 from the Ministry of Education, Science and Culture.

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