July, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 2381—2386 (1987) 2381

Application of Mössbauer Spectroscopy to a Structural Study of Superionic Conducting $AgI-Ag_2O-B_2O_3$ Glasses

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

(Received December 24, 1986)

A structural study of silver borate glasses containing 20 mol% AgI and 1 mol% $^{57}Fe_2O_3$ has been performed by Mössbauer spectroscopy. A Mössbauer spectrum of these glasses consists of an asymmetric quadrupole doublet with an isomer shift smaller than 0.4 mm s^{-1} with respect to metallic iron. This indicates that the individual Fe^{3+} ions are present at the substitutional sites of the tetrahedral boron atoms constituting BO_4 units as a network former. An increase in the Ag_2O content results in continuous decreases in the isomer shift and the quadrupole splitting when the Ag_2O content exceeds about 16 mol%, which corresponds to the Ag_2O/B_2O_3 ratio of 0.25 and the alkali oxide content of 20 mol% in the binary borate glasses. These results are ascribed to the formation of nonbridging oxygen atoms in the tetrahedral BO_4 and FeO_4 units. A glass transition temperature (T_g) of the glasses shows a distinct composition dependency, having a maximum around 16 mol% Ag_2O. These lead to the conclusions that planar BO_3 units are changed into the tetrahedral BO_4 units in the lower Ag_2O content region and that the nonbridging oxygen atoms are formed in the BO_4 and FeO_4 units when the Ag_2O content is higher than 16 mol%. These conclusions are well consistent with the composition dependency of the electric conductivity which shows a minimum when the Ag_2O content is 10—15 mol%.

Superionic conducting glasses have attracted much attention because of the scientific interest in the conduction mechanism as well as the high technological applicability. The electric conductivity of the superionic conducting glasses is known to reach the order of 10^{-2} S cm^{-1},[1-13] which is almost equivalent to that of the crystalline superionic conductor (solid state electrolytes) such as α-AgI and β-Al_2O_3. Comparing the magnitude of the electric conductivity of the superionic conducting glasses to that of ordinary oxide glasses such as borate and phosphate glasses, which is usually smaller than about 10^{-12} or 10^{-13} S cm^{-1},[14] it is easily understood that the former is extraordinary larger than the latter. The high electric conductivity of the superionic conducting glasses is assumed to be due to an "ion migration" of monovalent cations such as Ag^+, Li^+, and Na^+ which are present at the interstitial sites of the network structure. As for the role of the Ag^+ ions in the conduction mechanism of the superionic conducting glasses, Minami et al.[1,5,6] suggested the presence of two types of Ag^+ ions; those originated from AgX molecules (X=Cl, Br, and I) and those from Ag_2O molecules. The former is considered to be ionically bonded with the halide ions at the interstitial sites of the network structure, being primarily concerned with the electric (ionic) conduction. The latter is considered to be covalently bonded with oxygen atoms constituting a network structure and is less mobile than the former. Raman and EXAFS studies of the superionic conducting glasses revealed that the mobile Ag^+ ion is surrounded by four halide ions at the interstitial sites of network structure and is forming a microdomain or a distorted sublattice of α-AgI phase having a high electric conductivity.[9,10,12] On the other hand, Chiodelli et al.[13] ruled out the presence of the high electric conducting α-AgI phase dispersed in the glass network, for the electric conductivity of the silver borate glasses containing AgI shows a marked increase with increasing Ag_2O content when the AgI content is constant and also the conductivity of binary $Ag_2O-B_2O_3$ glasses is much higher than that of ordinary alkali borate glasses. The conductivity measurements of binary $Ag_2O-B_2O_3$ glasses performed by Matusita and Sakka[15] and Tsuchiya et al.[16] revealed that the conductivity of $30Ag_2O \cdot 70B_2O_3$ glass is about 10^{-6} S cm^{-1} at 100 °C and is higher than 10^{-8} S cm^{-1} at room temperature. These experimental results suggest that a part of the Ag^+ ions originating from Ag_2O also participate in the electric conduction. Tsuchiya et al.[16] ascribed the high conductivity of the $Ag_2O-B_2O_3$ glasses to an electron hopping from the colloidal Ag^0 to the Ag^+ ions. A structural study of the superionic conducting $AgCl-Ag_2O-B_2O_3$ glasses containing 1 mol% $^{57}Fe_2O_3$ has already been performed by means of Mössbauer spectroscopy,[17] where the present authors elucidated the relationship between the distinct composition dependency of the electric conductivity and the structural role of the Cl^- ions in those glasses. Namely the highest conductivity is observed when both the mobile and electric conducting Ag^+ ions and the Cl^- ions are present at the interstitial sites of the network structure, i.e. when the Ag_2O content is lower than about 10 mol% in the case of the silver borate glasses containing 20 mol% AgCl. Nishida et al.[17] also elucidated that the conductivity shows a distinct decrease when the Cl^- ions are incorporated into the network structure, as nonbridging chlorine atoms, of the borate glasses having the Ag_2O content higher than about 10 mol%. In these glasses, it was concluded that the mobility of the Ag^+ ions is depressed because of the increased chemical bond strength between the Ag^+ ion and the Cl^- ion when the latter ion is present as a nonbridging chlorine atom. This conclusion is consistent with those given by Minami et al.[1,5,6] that only the Ag^+ ions originating from AgX molecules (X=Cl, Br, and I) contribute to the electric conduction and that the Ag^+ ions originating from Ag_2O molecules are almost immobile. This will be the case for the Ag^+ ions linked with the nonbridging chlorine atoms in the network structure. In contrast to the distinct composition dependency of the structural role of the Cl^- and Br^- ions in borate glasses,[18–20] all the I^- ions are known to be present at the interstitial sites of the network structure irrespective of the composition of the borate glasses.[20] The I^- ions are quite different from the Cl^- or Br^- ions in terms of the nature of the chemical bond with the Ag^+ ions; the chemical bond between the Ag^+ and the I^- ions is known to be always ionic and therefore the mobility of the Ag^+ ions is expected not to be affected by the structural role of the I^- ions.

Because of the background described above, the present Mössbauer study was performed in order to elucidate the local structure of the silver borate glasses containing 20 mol% AgI. Mössbauer spectroscopy has so far been applied to the structural study of several borate glasses.[17–19,21–25] As a result, several conclusions have been obtained such as a formation of nonbridging oxygen, chlorine, and bromine atoms and a structural change from glass to glass-ceramics. These structural studies by means of Mössbauer spectroscopy suggest that the Mössbauer spectroscopy is a very effective method for the structural study of glasses and that small amounts of iron (Fe^{3+} and Fe^{2+}), which are used as a Mössbauer probe, are easily incorporated into the glasses either as a network former or as a network modifier. DTA measurements of the silver borate glasses containing 20 mol% Agl and 1 mol% Fe_2O_3 were also performed because glass transition temperature (T_g) is known to reflect the structural changes such as a change in the coordination number of network-forming atoms (network former) and a destruction or a depolymerization of the network structure due to a formation of nonbridging oxygen atoms.[26–34]

Experimental

Silver borate glasses containing 20 mol% AgI and 1 mol% Fe_2O_3 were prepared by fusing the individual mixtures of commercially available AgI, Ag_2O, B_2O_3, and $^{57}Fe_2O_3$, of a guaranteed reagent grade, at 1020 °C for 3 h in an electric muffle furnace. After the fusion in the ambient atmosphere, each melt in a platinum crucible was immediately quenched with ice-cold water. Mössbauer measurements of pulverized samples were performed by a constant acceleration method at room temperature using a proportional counter and a 1024 channel multichannel analyzer. Cobalt-57 (10 mCi) diffused into a palladium foil was used as the Mössbauer source. As a standard material for the isomer shift, a metallic iron foil enriched with iron-57 was used. The iron foil was also used for the velocity-calibration of the spectrometer. Each Mössbauer spectrum was analyzed into a quadrupole doublet with the same linewidth. DTA measurements of these glasses were performed ranging from room temperature to 700 °C with a heating rate of 5 °C min^{-1}. An Al_2O_3 powder was used as a standard material in the DTA measurements. Electric-conductivity measurements were performed at room temperature by applying a DC voltage of 3 V. Before the measurement, each glass sample was pressed into a pellet at a net pressure of 2.6×10^6 g cm^{-2}.

Results and Discussion

All the transparent silver borate glasses prepared in the present study change their color from yellowish brown to reddish brown with increasing Ag_2O content. This is the same as the case of the silver borate glasses containing 20 or 30 mol% AgCl and 1 mol% $^{57}Fe_2O_3$.[17] The composition dependency of the color may be due to the different sizes of the colloidal Ag^0 present at the interstitial sites of the glass network.[16] A Mössbauer spectrum of the silver borate glass denoted by $20AgI\cdot25Ag_2O\cdot54B_2O_3\cdot1Fe_2O_3$ is shown in Fig. 1. It is seen from Fig. 1 that the spectrum consists of an asymmetric quadrupole doublet due to high spin Fe^{3+} species [35,36] and that the absorption intensity of the lower energy peak due to $\pm1/2\leftrightarrow\pm1/2$ transition is higher than that of the higher energy peak due to $\pm1/2\leftrightarrow\pm3/2$ transition. The asymmetric spectrum is known to be caused by the anisotropic recoil-free fraction referred to as the "Goldanskii–Karyagin effect."[37,38] In the case of the borate glasses, the asymmetric Mössbauer spectra are often observed especially in the borate glasses with lower alkali oxide contents, where the fraction of the planar BO_3 units is generally known to be large. The asymmetric Mössbauer spectra may be caused by the anisotropic chemical bond strength in the B–O or Fe–O bonds constituting the BO_4 or FeO_4 tetrahedra, brought about by the presence of the planar BO_3 units at the neighboring sites. It is seen from Fig. 1 that the doublet peaks are a little broadened around the base line. This will be due to a magnetic relaxation effect because of the relatively low Fe^{3+} concentration in the glasses, although the magnetic relaxation effect is not so strong as to exhibit a hyperfine spectrum composed of six absorption lines. All the Mössbauer parameters of the silver borate glasses studied in the present paper are summarized in Table 1, from which it is seen that the isomer shifts are located in a range of 0.32—0.25 mm s^{-1}. As for the coordination number of iron in glasses, earlier works are reviewed by Kurkjian[39] and Coey.[40] Recent Mössbauer results on the structure of glasses are reviewed by Müller-Warmuth

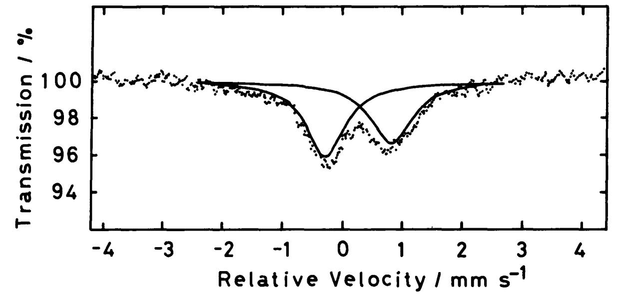

Fig. 1. Mössbauer spectrum of $20AgI \cdot 25Ag_2O \cdot 54B_2O_3 \cdot 1^{57}Fe_2O_3$ glass measured at room temperature.

Table 1. Mössbauer Parameters of the AgI-Ag_2O-B_2O_3 Glasses Containing 1 mol% $^{57}Fe_2O_3$

Composition	$\delta^{a)}$ mm s^{-1}	$\Delta^{b)}$ mm s^{-1}	$\Gamma^{c)}$ mm s^{-1}
$20AgI \cdot 5Ag_2O \cdot 74B_2O_3 \cdot 1Fe_2O_3$	0.31	1.20	0.88
$20AgI \cdot 10Ag_2O \cdot 69B_2O_3 \cdot 1Fe_2O_3$	0.31	1.19	0.93
$20AgI \cdot 13Ag_2O \cdot 66B_2O_3 \cdot 1Fe_2O_3$	0.32	1.17	0.91
$20AgI \cdot 15Ag_2O \cdot 64B_2O_3 \cdot 1Fe_2O_3$	0.31	1.15	0.97
$20AgI \cdot 20Ag_2O \cdot 59B_2O_3 \cdot 1Fe_2O_3$	0.28	1.14	0.93
$20AgI \cdot 25Ag_2O \cdot 54B_2O_3 \cdot 1Fe_2O_3$	0.26	1.10	0.82
$20AgI \cdot 30Ag_2O \cdot 49B_2O_3 \cdot 1Fe_2O_3$	0.25	1.11	0.83

a) Isomer shift. b) Quadrupole splitting. c) Linewidth.

and Eckert.[41] According to Coey,[40] most Fe^{3+} ions are known to occupy the tetrahedral sites in borate and silicate glasses. This is well consistent with the Mössbauer results of a series of alkali borate[17—19,21—25] and alkali borosilicate[42,43] glasses containing small amounts of Fe_2O_3, obtained by the present authors. In these Mössbauer studies,[17—19,21—25,42,43] all the isomer shifts proved to lie in a range of 0.38—0.22 mm s^{-1} with respect to metallic iron. (The experimental error for the isomer shift has usually been estimated to be ±0.01 mm s^{-1}.) Judging from the experimental results shown in the reviews[39—41] and the recent Mössbauer results on the structure of glasses performed by the present authors,[17—19,21—25,42,43] the isomer shift of the Fe^{3+} ions is concluded to be smaller than about 0.40 mm s^{-1} when they are tetrahedrally coordinated. On the other hand, octahedrally coordinated Fe^{3+} ions have been observed in several phosphate glasses,[44—46] where all the isomer shifts proved to be larger than 0.42 mm s^{-1}. Those experimental results lead to the conclusion that the criterion of the isomer shift, with respect to metallic iron, lies at about 0.40 mm s^{-1} for the tetrahedrally and octahedrally coordinated Fe^{3+} ions. The symmetries refer to "distorted" tetrahedral or octahedral configurations, for the bond lengths and the bond angles are more or less distributed in glasses. This is well reflected in the large linewidth values summarized in Table 1, where the linewidth is much larger than that of the ordinary crystalline compounds containing iron.[35,36] The large linewidth of the glasses studied in the present paper is partially due to the magnetic relaxation effect described above. The present Mössbauer results therefore suggest that most of the Fe^{3+} ions are present at the tetrahedral environments in the silver borate glasses. This indicates the presence of the tetrahedral FeO_4 units at the substitutional sites of the tetrahedral BO_4 units. It is considered that the Fe^{3+} ions are easily incorporated into the matrix of borate glasses. The substitution of the iron for the other metal or metalloid ions will easily occur in the high energy and nonequilibrium states when the glass samples are prepared by fusion.

The composition dependencies of the isomer shift and the quadrupole splitting of the Fe^{3+} ions are shown in Figs. 2 and 3, respectively. It is seen from Fig. 2 that the isomer shift shows a distinct decrease when the Ag_2O content exceeds about 16 mol%. A distinct decrease in the isomer shift of the Fe^{3+} ions has already been observed in alkali borate[21—25] and borosilicate[42,43] glasses when the alkali oxide (K_2O) content is higher than 20 and 8—10 mol%, respectively. In these glasses,[21—25,42,43] the decrease in the isomer shift of the Fe^{3+} ion, which is present at the substitutional site of the tetrahedral boron or silicon atoms, was ascribed to the formation of nonbridging oxygen atoms ($-O^-$) in the BO_4 or SiO_4 tetrahedral units, because the formation of the nonbridging oxygen atoms results in decreased interatomic distances in the B–O or Si–O bonds. This will be the case for the chemical bond length in the Fe–O bond. On the other hand, germanate glasses,[30,47] of which network structure is composed of GeO_4 and GeO_6 units, showed a drastic increase in the isomer shift of Sn^{4+} ions when nonbriding oxygen atoms are formed in the tetrahedral GeO_4 units. In the case of the ^{119}Sn-Mössbauer spectroscopy, an increase in the s-electron density at the tin nucleus results in an increase in the isomer shift. This is apparently opposite to the case of the ^{57}Fe-Mössbauer spectroscopy.[35,36] It should be noted that the formation of the nonbridging oxygen atoms in the GeO_4 tetrahedra was concluded through an increase in the isomer shift of the Sn^{4+} ions present at the interstitial sites of the network structure composed of the GeO_4 tetrahedra and the GeO_6 octahedra. These experimental results lead to the conclusion that the distinct decrease in the isomer shift shown in Fig. 2, observed when the Ag_2O content is equal to or higher than about 16 mol%, is due to the formation of nonbridging oxygen atoms in the tetrahedral BO_4 or FeO_4 units. This conclusion is consistent with the distinct and continuous decrease in the quadrupole splitting in the similar Ag_2O content region (Fig. 3). It is seen from Fig. 3 that the quadrupole splitting shows a distinct decrease when the Ag_2O content is equal to or higher than 15 mol%. As to the composition dependency of the quadrupole

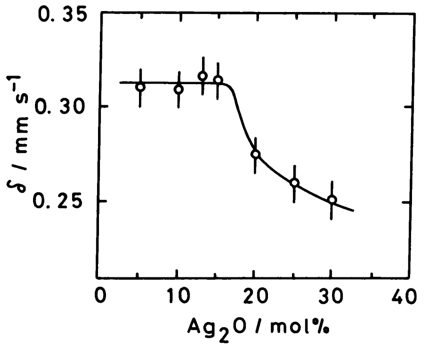

Fig. 2. Composition dependency of the isomer shift (δ) of the Fe^{3+} ions in the Ag_2O-B_2O_3 glasses containing 20 mol% AgI and 1 mol% $^{57}Fe_2O_3$.

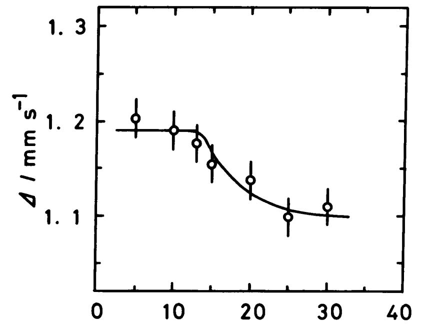

Fig. 3. Composition dependency of the quadrupole splitting (Δ) of the Fe^{3+} ions in the Ag_2O-B_2O_3 glasses containing 20 mol% AgI and 1 mol% $^{57}Fe_2O_3$.

splitting of the Fe^{3+} ions in glasses, distinct decreases have been observed when the nonbridging oxygen atoms are formed in alkali borate,[21–25] borosilicate,[42,43] and phosphate[45,46] glasses. The decrease in the quadrupole splitting of the Fe^{3+} ions is ascribed to an increased symmetry around the Fe^{3+} ions, because the Fe^{3+} ions of high spin state have a symmetric electron configuration of $3d^5$ in the outermost orbital and therefore only the electric field gradient brought about by the neighboring atoms or ions primarily affects the electric field gradient at the iron nucleus. Similar phenomenon has been observed in the case of potassium germanate glasses containing tin (Sn^{4+}), which also has a symmetric electron configuration of $4d^{10}$,[30,47] in spite that the Sn^{4+} ions are ionically present at the interstitial sites of the network structure. In the germanate glasses, the formation of nonbridging oxygen atoms was concluded to start when the alkali oxide content exceeds about 16 mol%. In the light of these reasons, the decrease in the quadrupole splitting of the Fe^{3+} ions observed in the present study is ascribed to the formation of nonbridging oxygen atoms in the tetrahedral BO_4 and FeO_4 units. (Each Fe^{3+} ion is concluded to be present at the substitutional site of the tetrahedral boron atom as described above.) These conclusions are well consistent with those obtained in the previous Mössbauer[21–25] studies of alkali borate glasses, i.e., the formation of nonbridging oxygen atoms in the BO_4 units starts when the alkali oxide content is equal to or higher than 20 mol%. The alkali oxide content of 20 mol% in the binary alkali borate glasses corresponds to about 16 mol% in the present ternary silver borate glass system containing 20 mol% AgI. (The Ag_2O/B_2O_3 ratio of 16/63 (=0.25) is consistent with the K_2O/B_2O_3 ratio of 20/80.) Effect of the Fe_2O_3 on the structure of the borate glasses can be neglected because the content is very low, i.e. 1 mol% in the present study and 0.33 mol% in the previous studies.[23,24] The same results have also been obtained in the borate glasses with the Fe_2O_3 content of 7 mol%.[21,22,25] These results suggest that the structure of the silver borate glasses is essentially the same as that of the alkali borate glasses and that the I^- ions are present at the interstitial sites of the network structure all over the compositional range studied in the present paper. This is obviously different from the case of the Cl^- and the Br^- ions which change their structural role from the interstitial anions to the nonbridging halogen atoms, depending on the composition.[17–20]

Each DTA curve of silver borate glasses containing 20 mol% AgI and 1 mol% Fe_2O_3 consists of a simple endothermic peak due to glass transition and one or two exothermic peak(s) due to crystallization. All the glass transition temperatures (T_g) obtained in the present study are shown in Fig. 4, where the T_g is plotted against the Ag_2O content of the glasses. DTA studies of several glasses have revealed that T_g shows a close relationship with a change in the coordination number of the network-forming atoms (network former) and with the formation of nonbridging oxygen or halogen atoms which means a destruction or depolymerization of the glass matrix.[17,26–34] In general. T_g shows a distinct increase when the coordination number of the network forming atoms increases. For example the change in the coordination

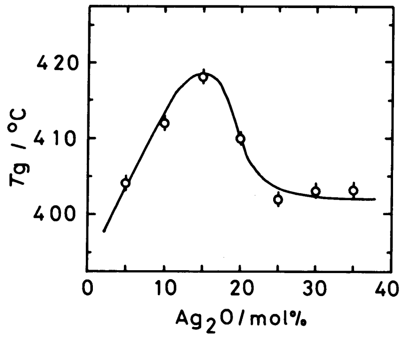

Fig. 4. Composition dependency of the glass transition temperature (T_g) of the Ag_2O-B_2O_3 glasses containing 20 mol% AgI and 1 mol% Fe_2O_3.

number of Ge from 4 to 6 in germanate glasses is observed as a continuous increase in the T_g.27,28,30) The increase in the T_g, observed with increasing Ag_2O content of the silver borate glasses in the lower Ag_2O content region (Fig. 4), is therefore ascribed to the well-known structural change from the BO_3 triangles to the BO_4 tetrahedra in the ordinary borate glasses, i.e. an increase in the coordination number of boron from 3 to 4. Contrary to this, the formation of nonbridging oxygen atoms results in a decrease in the T_g.27,28,30,34) These experimental results suggest that a decrease in the T_g, observed in the present silver borate glasses having the Ag_2O contents higher than 15 mol% (Fig. 4), is due to the formation of nonbridging oxygen atoms in the tetrahedral BO_4 or FeO_4 units. This is well consistent with the Mössbauer results described above.

Composition dependency of the electric conductivity is shown in Fig. 5a, from which it is seen that the conductivity of the silver borate glasses containing AgI shows a slight increase with increasing Ag_2O content when the Ag_2O content exceeds about 15 mol%. This is very contrary to the composition dependency of the silver borate glasses containing the same amount (20 mol%) of AgCl,17) shown with a broken line (Fig. 5b). In the silver borate glasses containing 20 mol% AgCl and 1 mol% $^{57}Fe_2O_3$,17) the drastic decrease in the conductivity was ascribed to the decreased number of the mobile Ag^+ ions present at the interstitial sites of the network structure, brought about as a result of the change in the structural role of the Cl^- ions. (Most of the Cl^- ions were concluded to change their structural role from the interstitial anions to the nonbridging chlorine atoms when the Ag_2O content exceeds about 10 mol%.17)) Also, the decrease in the mobility of the electric conducting Ag^+ ions was concluded to be due to the increased chemical bond strength between the Ag^+ ions and the nonbridging chlorine atoms.17) Judging from the structural information on the silver borate glasses containing 20 mol% AgI, obtained from the Mössbauer and DTA measurements in the present study, the slight increase in the conductivity observed with increasing Ag_2O content (Fig. 5a) is ascribed to the open structure of the borate glasses brought about as a result of the formation of nonbridging oxygen atoms in the tetrahedral BO_4 (or FeO_4) units. This means a destruction of the complicated network structure composed of the planar BO_3 and the tetrahedral BO_4 (and FeO_4) units linked with bridging oxygen atoms. In these glasses, the mobility of the Ag^+ ions will be enhanced because of the decreased physical and chemical interactions between the Ag^+ and the glass matrix. These results are well consistent with the general rule that the ionic conduction in solids is enhanced when the electric charge and the ionic radius of cations are small and the size of space or "tunnel," where the conducting ions actually pass through under an electric field, is large enough. This is also the case for the decrease in the electric conductivity observed in the Ag_2O content region lower than about 15 mol% (Fig. 5a), since the increase in the Ag_2O or alkali oxide contents results in a structural change from the planar BO_3 to the tetrahedral BO_4 units, as described above. This structural change will bring about a more complicated network structure of the borate glasses compared to that of the original boric (B_2O_3) glass having only the planar BO_3 units. The complicated structure will result in a decreased mobility of the electric conducting Ag^+ ions.

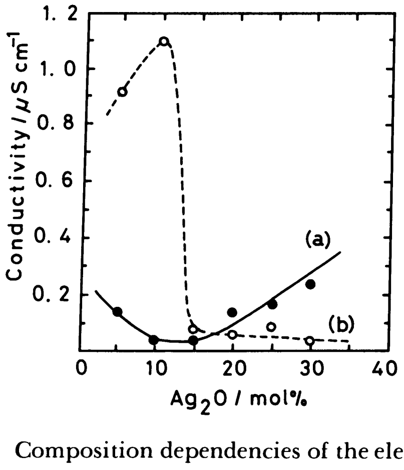

Fig. 5. Composition dependencies of the electric conductivity of the Ag_2O–B_2O_3 glasses containing (a) 20 mol% AgI and 1 mol% Fe_2O_3, and (b) 20 mol% AgCl and 1 mol% Fe_2O_3.17)

The authors are indebted to Mr. Toshiharu Hirai of Chemical and Catalysis Industrial Corporation for his kind help in the electric conductivity measurements. One of the authors (TN) is grateful to the Itoh Science Foundation and Grants-in-Aid for Scientific Research (Nos. 60740234 and 61740350) from the Ministry of Education, Science and Culture, for the financial support.

References

1) T. Minami, Y. Takura, and M. Tanaka *J. Electrochem. Soc.*, **124**, 1659 (1977).

2) J. P. Malugani, A. Wasniewski, M. Doreau, G. Robert, and A. Rikabi, *Mater. Res. Bull.*, **13**, 427 (1978).

3) T. Minami and M. Tanaka, *Rev. Chim. Miner.*, **16**, 283 (1979).

4) A. Magistris, G. Chiodelli, and A. Schiraldi, *Electrochim. Acta*, **24**, 203 (1979).

5) T. Minami and M. Tanaka, *J. Non-Cryst. Solids*, **38/39**, 289 (1980).

6) T. Minami, K. Imazawa, and M. Tanaka *J. Non-Cryst. Solids*, **42**, 469 (1980).

7) J. P. Malugani, G. Robert, and R. Mercier, *Mater. Res. Bull.*, **15**, 715 (1980).

8) G. Chiodelli, A. Magistris, M. Villa, and J. L. Bjorkstam, *Mater. Res. Bull.*, **17**, 1 (1982).

9) A. Fontana, G. Mariotto, E. Cazzanelli, G. Carini, M. Cutroni, and M. Federico, *Phys. Lett. A*, **93**, 209 (1983).

10) G. Dalba, A. Fontana, P. Fornasini, G. Mariotto, M. R. Masullo, and F. Rocca, *Solid State Ionics*, **9/10**, 597 (1983).

11) J. P. Malugani, R. Mercier, B. Fahys, and G. Robert, *J. Solid State Chem.*, **45**, 309 (1982).

12) J. P. Malugani and R. Mercier, *Solid State Ionics*, **13**, 293 (1984).

13) G. Chiodelli, G. Camparivigano, G. Flor, A. Magistris, and M. Villa, *Solid State Ionics*, **8**, 311 (1983).

14) L. Murawski, *J. Mater. Sci.*, **17**, 2155 (1982).

15) K. Matusita and S. Sakka, *Yogyo Kyokai Shi*, **84**, 496 (1976).

16) T. Tsuchiya, T. Horiuchi, and T. Moriya, *Yogyo Kyokai Shi*, **87**, 223 (1979).

17) T. Nishida, M. Ogata, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **59**, 2401 (1986).

18) T. Nishida, N. Kai, Y. Takashima, *Phys. Chem. Glasses*, **22**, 107 (1981).

19) T. Nishida, T. Nonaka, T. Isobe, and Y. Takashima, *Phys. Chem. Glasses*, **24**, 88 (1983).

20) T. Maekawa, S. Satoh, and T. Yokokawa, *Yogyo Kyokai Shi*, **93**, 20 (1985).

21) T. Nishida and Y. Takashima, *J. Non-Cryst. Solids*, **37**, 37 (1980).

22) T. Nishida, Y. Takashima, and Y. Nakayama, *J. Solid State Chem.*, **33**, 141 (1980).

23) T. Nishida, T. Shiotsuki, and Y. Takashima, *J. Non-Cryst. Solids*, **41**, 161 (1980).

24) T. Nishida, T. Hirai, and Y. Takashima, *J. Non-Cryst. Solids*, **43**, 221 (1981).

25) T. Nishida and Y. Takashima, "Application of Mössbauer Effect on the Crystallization of Several Glasses," in "Industrial Applications of the Mössbauer Effect," ed by G. J. Long and J. Stevens, Plenum Publ. Corp., New York (1987), pp. 409—422.

26) E. M. Boulos and N. J. Kreidl *J. Am. Ceram. Soc.*, **54**, 368 (1971).

27) J. E. Shelby, *J. Am. Ceram. Soc.*, **57**, 436 (1974).

28) J. E. Shelby *J. Appl. Phys.*, **46**, 193 (1975).

29) R. M. Almeida and J. D. Mackenzie, *J. Chem. Phys.*, **74**, 5954 (1981).

30) T. Nishida, M. Katada, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **57**, 3566 (1984).

31) J. L. Piguet and J. E. Shelby, *J. Am. Ceram. Soc.*, **68**, 450 (1985).

32) T. Nishida, T. Nonaka, and Y. Takashima, *Bull, Chem. Soc. Jpn.*, **58**, 2255 (1985).

33) T. Nishida and Y. Takashima *Bull. Chem. Soc. Jpn.*, **59**, 2789 (1986).

34) T. Nishida and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **60**, 941 (1987).

35) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy," Chapman and Hall Ltd., London (1971) Chap. 3.

36) R. Ingalls, F. Van der Woude, and G. A. Sawatzky, "Iron and Nickel," in "Mössbauer Isomer Shifts," ed by G. K. Shenoy and F. E. Wagner, North-Holland Pub Co., Amsterdam (1978), Chap. 7.

37) V. I. Goldanskii, G. M. Gorodinskii, S. V. Karyagin, L. A. Korytko, L. M. Krizhanskii, E. F. Makarov, I. P. Suzdalev, and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, **147**, 127 (1962).

38) S. V. Karyagin, *Dokl. Akad. Nauk SSSR*, **148**, 1102 (1963).

39) C. R. Kurkjian, *J. Non-Cryst. Solids*, **3**, 157 (1970).

40) J. M. D. Coey, *J. Phys.*, **35**, C6—89 (1974).

41) W. Müller-Warmuth and H. Eckert, *Phys. Rep.*, **88**, 91 (1982).

42) T. Nishida, T. Hirai, and Y. Takashima, *Phys. Chem. Glasses*, **22**, 94 (1981).

43) T. Nishida, T. Hirai, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **54**, 3735 (1981).

44) M. F. Taragin, J. C. Eisenstein, and W. Heller, *Phys. Chem. Glasses*, **13**, 29 (1972).

45) T. Nishida, T. Shiotsuki, and Y. Takashima, *J. Non-Cryst. Solids*, **43**, 115 (1981).

46) T. Nishida, T. Shiotsuki, and Y. Takashima, *J. Non-Cryst. Solids*, **43**, 123 (1981).

47) T. Nishida, M. Katada, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **58**, 1745 (1985).