Mössbauer and DTA Studies of Superionic Conducting AgCl-Ag_2O-B_2O_3 Glasses

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A structural study of silver borate glasses containing 20 or 30 mol% AgCl and 1 mol% Fe_2O_3 has been performed by means of Mössbauer spectroscopy. The distinct decreases in the Mössbauer parameters observed in the borate glasses with Ag_2O contents higher than about 10 mol% suggest that chloride ions are covalently bonded with tetrahedral iron or boron atoms as nonbridging chlorine. On the other hand, chloride ions are considered to be ionically bonded with Ag^+ ions at the interstitial sites of the three-dimensional network composed of BO_3, BO_4, and FeO_4 units when the Ag_2O content is lower than 10 mol%. Measurements of the glass transition temperatures and the electric conductivity show a good agreement with the Mössbauer results, suggesting that mobile and electric conducting Ag^+ ions change their configurational sites from the interstitial sites which are close to Cl^- ions to different interstitial sites which are close to the nonbridging chlorine atom.

Superionic conducting glasses containing Ag^+ ions have attracted much attention because of the scientific interest in the conduction mechanism as well as their technological applications.[1-13] The high electric conductivity of these glasses, amounting to the order of 10^{-2} S cm^{-1}, has been reported to be brought about by a cation conduction due to mobile Ag^+ ions which are considered to be present at interstitial sites of the glass-network structure. (The electric conductivity of ordinary alkali oxide glasses is known to be lower than 10^{-13} or 10^{-14} S cm^{-1}.) Minami et al.[1,5,6] suggested that mobile Ag^+ ions originate from AgX (X=Cl, Br, and I) molecules and that the nature of the chemical bond between the mobile Ag^+ ion and the neighboring halide ion is completely ionic. They also suggested that the nature of the chemical bond between the Ag^+ ion originating from Ag_2O and the oxygen atom constituting the skeleton of the glass network is partially covalent. This is different from the ionic bond between the alkali metal ion and the oxygen in ordinary alkali oxide glasses. In the light of this suggestion, the latter type of Ag^+ ion has been considered to be essentially immobile. Raman and EXAFS studies of the superionic conducting glasses revealed that the mobile Ag^+ ion is tetrahedrally surrounded by four halide ions at the interstitial site, forming a microdomain or a distorted sublattice of the α-AgI phase which itself has a high electric conductivity.[9,10,12] On the other hand, Chiodelli et al.[13] ruled out the presence of a high electric-conducting α-AgI phase dispersed in the glass network, for the electric conductivity of silver borate glasses containing AgI also shows a marked increase with the 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 electric conductivity measurements of binary Ag_2O–B_2O_3 glasses performed by Matusita and Sakka[14] and by Tsuchiya et al.[15] revealed that the conductivity of $30Ag_2O \cdot 70B_2O_3$ glass is about 10^{-6} S cm^{-1} at 100 °C and that it is higher than 10^{-8} S cm^{-1} at room temperature. These experimental results seem to lead to the tentative conclusion that at least a part of the Ag^+ ions originating from Ag_2O also participate in the electric conduction. One possible explanation of the high electric conductivity of binary silver borate glasses is the electron hopping from the colloidal Ag^0 to the Ag^+ ions originating from Ag_2O.[15]

Mössbauer spectroscopy has been successfully used for the structural study of several glasses, such as borate,[16-20] borosilicate,[21,22] phosphate,[23,24] borophosphate,[25] germanate,[26,27] KCl–$ZnCl_2$,[28] and BaF_2–ZrF_4[29] glasses. Mössbauer and ESR studies of potassium borate glasses containing a small amount of KCl or KBr revealed that chloride and bromide ions are ionically present at interstitial sites of the three-dimensional network composed of BO_3 and BO_4 units when the alkali oxide (K_2O) content is lower than 15 mol%.[19,20] On the other hand, the chloride and bromide ions proved to be covalently bonded with tetrahedal boron or iron (Fe^{3+}), as nonbridging chlorine (–Cl) and bromine (–Br) atoms respectively, when the K_2O content is higher than 15 mol%.[19,20] These results are almost entirely consistent with the optical absorption results reported by Maekawa et al.[30]

The present Mössbauer study was carried out in order to elucidate the local structure of superionic conducting AgCl–Ag_2O–B_2O_3 glasses, for Mössbauer spectroscopy is a very useful method for the structural study of amorphous materials, the structural study of which is very difficult by means of ordinary diffraction methods. The differential thermal analysis (DTA) of these glasses was performed because any change in the local structure of glasses, such as a change in the coordination number of network-forming atoms or the formation of nonbridging atoms, is known to be well reflected in the glass transition temperature (T_g).[26,29,31-35]

Experimental

Silver borate glasses containing 20, 30, and 40 mol% AgCl and 1 mol% Fe_2O_3 were prepared by fusing the individual mixtures of AgCl, Ag_2O, B_2O_3, and $^{57}Fe_2O_3$, of a guaranteed reagent grade, at 1020 °C for 3 h using an electric muffle furnace. After the fusion, each melt in a platinum crucible was quenched with ice-cold water. The yellowish brown to reddish brown glasses obtained in this way were pulverized for the Mössbauer, DTA, and electric-conductivity measurements. Mössbauer measurements were performed by means of a constant-acceleration method at room temperature. Cobalt-57 (10 mCi) diffused into a palladium foil and a metallic iron foil enriched with iron-57 were used as the Mössbauer source and the reference for the isomer shift respectively. The velocity of the spectrometer was calibrated with the spectrum of metallic iron foil. Using a least-squares method, each Mössbauer spectrum was analyzed into a quadrupole doublet with the same width and the same intensity. DTA measurements were performed at a heating rate of 5 °C min^{-1} over the range from room temperature to 700 °C, and Al_2O_3 powder was used as the standard material. Electric-conductivity measurements for each glass sample (600 mg), pressed at a net pressure of 2.6×10^6 g cm^{-2}, were performed at room temperature by applying a DC voltage of 3 V.

Results and Discussion

The Mössbauer measurements of $AgCl-Ag_2O-B_2O_3$ glasses containing 1 mol% Fe_2O_3 revealed that iron is present only in the Fe^{3+} state, as is shown in Fig. 1. It may also be seen from Fig. 1 that the spectrum consists of a quadrupole doublet caused by the electric field gradient at the iron nucleus. Quadrupole doublets are often observed in the Mössbauer spectra of borate glasses,[16–20] and the increase in the quadrupole splitting of Fe^{3+} suggests the decreased symmetry of FeO_4 tetrahedra, because high-spin Fe^{3+} species have a symmetric $3d^5$ electron configuration in the outermost orbital. Therefore, only the electric field gradient brought about by the neighboring atoms or ions, i.e., oxygen atoms in the oxide glasses, affects the quadrupole splitting values. The symmetry of the BO_4 tetrahedra will also be reflected in the magnitude of the quadrupole splitting, for all the Fe^{3+} ions are considered to be present at the substitutional sites of the boron atoms constituting the BO_4 tetrahedra. (The isomer shifts smaller than ca. 0.4 mm s^{-1} mean that each Fe^{3+} ion is surrounded by four oxygen atoms, just as in the case of the boron atoms constituting the BO_4 tetrahedra.) It may be seen from Fig. 1 that the linewidth (FWHM) of the Fe^{3+} absorption is much larger than those of the Fe^{2+} or Fe^{3+} absorptions in the ordinary crystalline compounds, which is usually smaller than ca. 0.4 mm s^{-1} in the case of ^{57}Fe-Mössbauer spectroscopy. The large linewidth of the Fe^{3+} absorption in the borate glasses suggests that the Fe–O (and B–O) bond lengths and also the O–Fe–O (and O–B–O) bond angles are distributed. These distributions can be described as characteristic of amorphous materials. All the Mössbauer parameters obtained in the present study are summarized in Table 1, in which the isomer shifts of Fe^{3+} are in the range of 0.27 to 0.33 mm s^{-1} and show a slight decrease with an increase in the Ag_2O content. Table 1 indicates that quadrupole splitting also decreases with an increase in the Ag_2O content. (The experimental error for the isomer shift is estimated to be ±0.01 mm s^{-1}, and the errors for the quadrupole splitting and the linewidth are estimated to be ±0.02 mm s^{-1}.) The changes in the isomer shift and the quadrupole splitting with the Ag_2O content are also shown in Figs. 2 and 3 respectively.

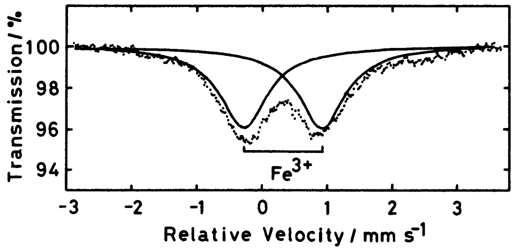

Fig. 1. Mössbauer spectrum for $20AgCl\cdot10Ag_2O\cdot69B_2O_3\cdot Fe_2O_3$ glass.

Table 1. Mössbauer Parameters for $AgCl-Ag_2O-B_2O_3$ Glasses

Composition	$\delta^{a)}$	$\Delta^{b)}$	$\Gamma^{c)}$
	mm s^{-1}	mm s^{-1}	mm s^{-1}
$20AgCl\cdot5Ag_2O\cdot74B_2O_3\cdot Fe_2O_3$	0.33	1.28	0.88
$20AgCl\cdot10Ag_2O\cdot69B_2O_3\cdot Fe_2O_3$	0.32	1.19	0.91
$20AgCl\cdot15Ag_2O\cdot64B_2O_3\cdot Fe_2O_3$	0.30	1.15	0.92
$20AgCl\cdot20Ag_2O\cdot59B_2O_3\cdot Fe_2O_3$	0.30	1.11	0.88
$20AgCl\cdot25Ag_2O\cdot54B_2O_3\cdot Fe_2O_3$	0.30	1.09	0.84
$20AgCl\cdot30Ag_2O\cdot49B_2O_3\cdot Fe_2O_3$	0.30	1.09	0.87
$30AgCl\cdot5Ag_2O\cdot64B_2O_3\cdot Fe_2O_3$	0.30	1.28	0.91
$30AgCl\cdot10Ag_2O\cdot59B_2O_3\cdot Fe_2O_3$	0.28	1.08	0.86
$30AgCl\cdot15Ag_2O\cdot54B_2O_3\cdot Fe_2O_3$	0.27	1.09	0.86
$30AgCl\cdot20Ag_2O\cdot49B_2O_3\cdot Fe_2O_3$	0.28	1.09	0.84
$30AgCl\cdot25Ag_2O\cdot44B_2O_3\cdot Fe_2O_3$	0.27	1.09	0.82

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

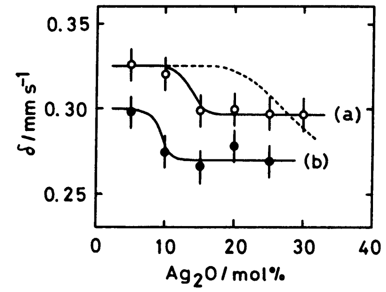

Fig. 2. Isomer shifts of Fe^{3+} in silver borate glasses containing (a) 20 mol% and (b) 30 mol% AgCl. A broken line refers to the change in the isomer shift of Fe^{3+} in $K_2O-B_2O_3$ glasses.[16,18]

Figure 2 demonstrates distinct decreases in the isomer shift of Fe^{3+} when the Ag_2O contents are in the ranges of 10—15 mol% and 5—10 mol% in the borate glasses containing 20 and 30 mol% AgCl respectively. The broken line shown in Fig. 2 refers to a change in the isomer shift of Fe^{3+} in the K_2O–B_2O_3 glasses, from which the formation of a nonbridging oxygen (NBO) atom in BO_4 and FeO_4 units can be deduced when the K_2O content is equal to or higher than 20 mol%.[16,18] In the Mössbauer and ESR studies of K_2O–B_2O_3 glasses containing a small amount of KCl or KBr, the formation of nonbridging chlorine or bromine atoms was concluded on the basis of the distinct decreases in the isomer shift of Fe^{3+} and the ESR absorption intensity of Cl_2^- and Br_2^- when the K_2O content is equal to or higher than 15 mol%.[19,20] These results suggest that the formation of nonbridging chlorine atom starts when the Ag_2O content is higher than about 10 mol% in the case of silver borate glasses containing 20 or 30 mol% AgCl. The critical composition of the ternary AgCl–Ag_2O–B_2O_3 glass, where a distinct change in the isomer shift is observed, is found to be almost identical with the composition of the binary K_2O–B_2O_3 glass containing only 0.63 mol% KCl[19,20] when the Ag_2O/B_2O_3 molar ratio is compared to the K_2O/B_2O_3 ratio. That is, the molar ratio of 15/85 (=0.18) in the K_2O–B_2O_3 glass,[19,20] where it was concluded that the formation of the nonbridging chlorine atom starts, corresponds to the Ag_2O contents of about 12 and 10.5 mol% in the AgCl–Ag_2O–B_2O_3 glasses containing 20 and 30 mol% AgCl respectively. These conclusions are consistent with the results of the quadrupole splitting shown in Fig. 3, from which it is obvious that the quadrupole splitting shows a drastic decrease when the Ag_2O content is equal to or higher than 10 mol%. The broken line shown in Fig. 3 refers to a change in the quadrupole splitting of Fe^{3+} in the K_2O–B_2O_3 glasses;[16] the distinct decrease in the quadrupole splitting when the K_2O content is higher than 20 mol% is ascribed to the formation of a nonbridging oxygen atom in BO_4 and FeO_4 tetrahedral units, as has been described above. The increased quadrupole splittings of Fe^{3+} in the AgCl–Ag_2O–B_2O_3 glasses are ascribed to the substitution of the chloride ion for one of the oxygen atoms constituting the BO_4 or FeO_4 tetrahedra, or to the decreased symmetry of FeO_4 when the Ag_2O content is very low. Similar overall increases in the quadrupole splitting of Fe^{3+} have been observed in K_2O–B_2O_3 glasses containing a small number of chloride ions.[19]

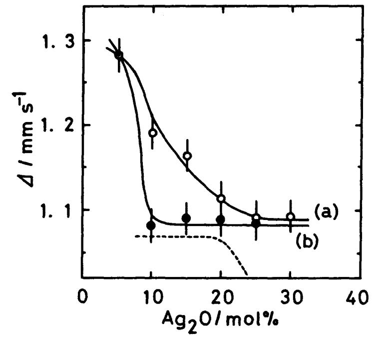

Fig. 3. Quadrupole splittings of Fe^{3+} in silver borate glasses containing (a) 20 mol% and (b) 30 mol% AgCl. A broken line refers to the change in the quadrupole splitting of Fe^{3+} in K_2O–B_2O_3 glasses.[16]

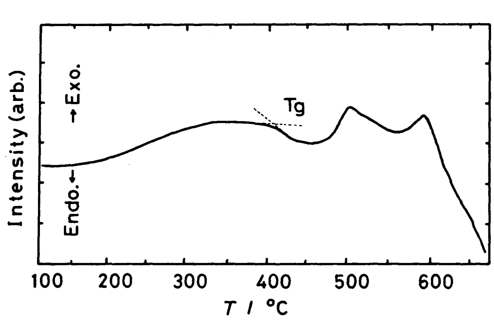

Fig. 4. DTA curve for 20AgCl·10Ag_2O·69B_2O_3·Fe_2O_3 glass.

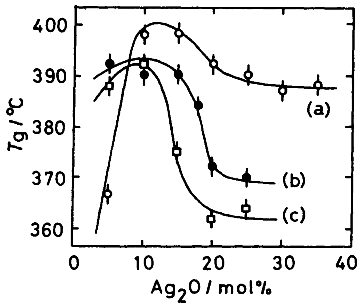

Fig. 5. Glass transition temperatures of silver borate glasses containing (a) 20 mol%, (b) 30 mol%, and (c) 40 mol% AgCl.

DTA measurements were performed for all the glass samples prepared in the present study. The DTA curve consists of a broad exothermic peak, followed by an endothermic peak and a few exothermic peaks due to crystallization (Fig. 4). As is shown in Fig. 4, the glass transition temperature (T_g) is generally obtained from the intersection of the tangent to the broad exothermic peak and that to the following endothermic peak. All the glass transition temperatures obtained in this way are shown in Fig. 5, in which T_g shows a maximum when the Ag_2O content is about 10 mol%. It is already known that the increased coordination number of network-forming boron and germanium, in borate and germanate glasses respectively, is well reflected in the gradual increase in T_g.[26,31–35] This is probably due to the increased degree of bridging in the glass skeleton as a result of the step-by-step structural changes from BO_3 to BO_4 units and from GeO_4 to GeO_6 units in borate and germanate glasses respectively. On the other hand, the formation of nonbridging oxygen atom, i.e., a decreased degree of bridging in the glass skeleton, is known to result in a decrease in T_g.[26,34,35] Therefore, the gradual decrease in the T_g observed in the silver borate glasses with the Ag_2O contents higher than about 10 mol% is concluded to be due to the formation of a nonbridging chlorine atom in BO_4 or FeO_4 units, i.e., the formation of BO_3Cl or FeO_3Cl units.

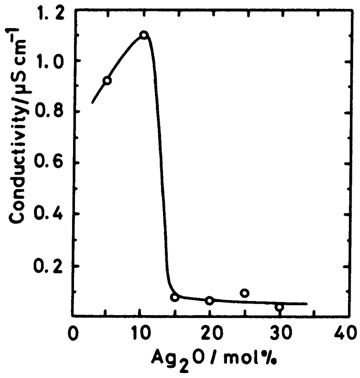

Fig. 6. Electric conductivities of silver borate glasses containing 20 mol% AgCl.

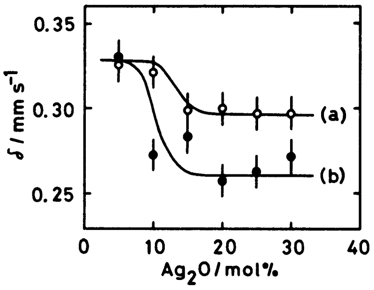

Fig. 7. Isomer shifts of Fe^{3+} in silver borate glasses containing 20 mol% AgCl. (a): Non-irrad., (b): irrad. with ^{60}Co-γ rays of 10^8 R.

This conclusion is consistent with the Mössbauer results presented above. An overall decrease in T_g with an increase in the AgCl content also supports this conclusion, because the number of nonbridging chlorine atoms will, to some extent, be proportional to the concentration of chloride ions in glasses.

The composition dependency of electric conductivity for silver borate glasses containing 20 mol% AgCl is shown in Fig. 6, which also shows a drastic change when the Ag_2O content exceeds about 10 mol%. Considering the experimental findings that the electric conductivity for binary Ag_2O–B_2O_3 glasses shows a drastic and almost linear increase with an increase in the Ag_2O content,[13–15] the remarkable decrease in the electric conductivity shown in Fig. 6 is concluded to be caused by AgCl. The drastic decrease in the electric conductivity suggests that the number of mobile Ag^+ ions decreases abruptly when the Ag_2O content exceeds about 10 mol% in the case of silver borate glasses containing 20 mol% AgCl. Considering the Mössbauer (Figs. 2 and 3) and DTA (Fig. 5) results presented above, this phenomenon can be correlated with the formation of nonbridging chlorine atoms in the silver borate glasses with an Ag_2O content higher than about 10 mol%. The number of mobile Ag^+ ions will be reduced because most of the Ag^+ ions, which were present with Cl^- ions at the interstitial sites of the three-dimensional network structure, follow the nonbridging chlorine atoms. As a result, such Ag^+ ions will become less mobile, just like the Ag^+ ions originating from Ag_2O molecules. These results are consistent with the prediction made by Minami et al.[1,5,6] that the electric conduction in AgX–Ag_2O–B_2O_3 glasses is primarily made by Ag^+ ions originating from AgX molecules. (X indicates Cl, Br, and I, as has been described above.) Their prediction will be especially valid in an Ag_2O content region in which most chloride ions are present at the interstitial sites of the three-dimensional network structure, i.e., when the Ag_2O content is lower than about 12 and 10.5 mol% in the cases of the silver borate glasses containing 20 and 30 mol% AgCl respectively. In the case of AgI–Ag_2O–B_2O_3 glasses, somewhat different results will be obtained, because the structural behavior of the I^- ion has been reported to be independent of the Ag_2O content of the glasses,[30] being contrary to the behavior of the Cl^- or Br^- ions.

Gamma-Ray irradiation experiments with silver borate glasses containing 20 mol% AgCl were performed in order to confirm the presence of nonbridging chlorine atoms in the silver borate glasses when the Ag_2O content is higher than about 10 mol%. According to the Mössbauer studies of γ-ray irradiated borate or borosilicate glasses, the irradiation is known to result in a decrease in the isomer shift of Fe^{3+} when a nonbridging oxygen atom is present in FeO_4 or BO_4 tetrahedral units.[21,36] Figure 7 shows the irradiation-induced changes in the isomer shift of Fe^{3+} in silver borate glasses containing 20 mol% AgCl. Gamma-Ray irradiations of 10^6 and 10^7 R result in gradual decreases in the isomer shifts, which are intermediate between the (a) and (b) curves. The gamma-ray irradiation of borate glasses is known to result in a reduction of Fe^{3+} to Fe^{2+} when the total iron content of the glasses is very low.[11,36] The decrease in the isomer shift shown in Fig. 7 is, therefore, ascribed to an increased s-electron density at the iron nucleus as a result of the charge transfer from a nonbridging chlorine atom to the neighboring iron atom constituting a FeO_3Cl tetrahedral unit. This will also be the case for a tetrahedral BO_3Cl unit.

All the experimental results obtained in the present study lead to the following conclusions. Chloride ions in AgCl–Ag_2O–B_2O_3 glasses are ionically bonded with Ag^+ ions at the interstitial sites of the three-dimensional network composed of BO_3 and BO_4 (and FeO_4) units when the Ag_2O content is lower than about 10 mol%, i.e., when the Ag_2O/B_2O_3 ratio is smaller than 15/85. On the other hand, chloride ions are covalently bonded with tetrahedral boron (or iron) atoms as nonbridging chlorine when the Ag_2O content exceeds about 10 mol%. These structural changes are concluded to affect the steric configuration of the Ag^+ ion, which is a cation conductor. That is, Ag^+ ions are considered to change their structural sites from the interstitial sites which are close to the Cl^- ions to different interstitial sites which are close to the nonbridging chlorine atoms. The latter type of Ag^+ ions seems to be less mobile than the former, because a drastic decrease in the electric conductivity is observed when the Ag_2O content exceeds about 10 mol%.

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