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Mixed Anion Effect on Conductivity of the Glasses in the System AgI-Ag_2MoO_4-$AgPO_3$

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The AgI-Ag_2MoO_4-$AgPO_3$ glasses were prepared and their silver ion conducting properties were investigated. An enhancement of conductivity was observed in the glasses containing two kinds of oxosalts at a constant AgI content. The enhancement of conductivity was closely related to the structural change of oxoanions included in the glasses.

Superionic conducting glasses, which show high ion conductivities in the range of 10^0 - 10^{-2} Sm^{-1} at room temperature, have extensively been investigated for their potential applications to solid state batteries, electrochromic devices, sensors, and so on. Recently some papers[1-4] have reported the "mixed anion effect" and/or "mixed former effect"; i.e. a positive deviation from additivity in the ion conductivity is observed in the glasses containing two kinds of anion species and/or of glass formers. This phenomenon shows a good contrast to the well known "mixed cation effect"; i.e. the conductivity of glasses shows the negative deviation from additivity, when two kinds of cation species, which are main carriers for electrical conduction, are mixed. The "mixed anion effect" and/or "mixed former effect" is a subject of interest to see the reason for the phenomenon itself and also to obtain glasses with the high ion conductivity, since not all the glasses containing two kinds of anion species and/or glass formers show the enhancement of conductivity. We assume that the enhancement of conductivity closely relates to the structural change of glasses with mixing two kinds of anion species and/or glass formers. Thus we try to prepare silver ion conducting glasses containing two kinds of oxosalts in the system AgI-Ag_2MoO_4-$AgPO_3$.

For sample preparation, AgI, Ag_2O, MoO_3 and $AgPO_3$ were used as raw materials. Mixtures of desired amounts of the raw materials were melted in a silica tube at 1053 K, and the melt was quenched onto an iron plate. The glass compositions were shown by the starting batch composition in mol%.

The FT-IR spectra were recorded on a Nicolet 20DXB FT-IR spectrophotometer in the range of 4000 - 400 cm^{-1} at room temperature; the measurements were carried out by use of the blown film method.[5] Ionic conductivity measurements were carried out for the bulk glasses with evaporated gold electrodes in a dry nitrogen atmosphere under 5 Hz to 500 kHz by use of a vector impedance meter(Hewlett-Packard 4800A) in the temperature range of

220 to 320 K. The conductivities were determined by employing the complex impedance analysis.

The glass-forming region in the ternary system AgI-Ag_2MoO_4-$AgPO_3$ is shown in Fig. 1. In the figure open circles, open triangles and closed circles denote glassy, partial crystalline and crystalline sample, respectively.

Figure 2 shows the FT-IR spectra of the glasses 60AgI•(40-x) Ag_2MoO_4•x$AgPO_3$ over the wavenumber range of 1400 - 400 cm^{-1}. The compositions of these glasses lie on the horizontal line in Fig. 1, i.e. they have a constant AgI content(60 mol%) and various mole ratios of molybdate to phosphate: (a) - (e) are the spectra of 60AgI•(40-x)Ag_2MoO_4•x$AgPO_3$ glasses, of which the $AgPO_3$ content increases from (a) to (e). In the range of 4000 - 1400 cm^{-1} there were no characteristic absorption bands.

The spectrum (a) is of the 60AgI•40Ag_2MoO_4 glass, where there are two absorption bands at 875 and 795 cm^{-1} assigned respectively to the ν_1 and the ν_3 modes of monomeric tetrahedral MoO_4^{2-} ions. This result indicates that the IR active species in the 60AgI•40Ag_2MoO_4 glass are monomer MoO_4^{2-} ions only and thus suggests that this glass consists of only monomer MoO_4^{2-} ions, I^- ions, and Ag^+ ions.

In the spectrum (e) of the 60AgI•40$AgPO_3$ glass, there are six absorption bands at about 1225, 1050, 890, 770, 510, and 470 cm^{-1}. The strong absorption bands at 1225 and 1050 cm^{-1}

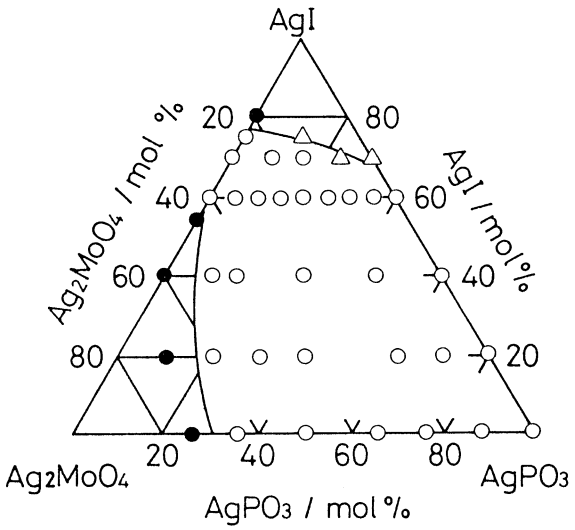

Fig. 1. Glass-forming region in the system AgI-Ag_2MoO_4-$AgPO_3$; (o) glassy, (△) partially crystalline, (●) crystalline.

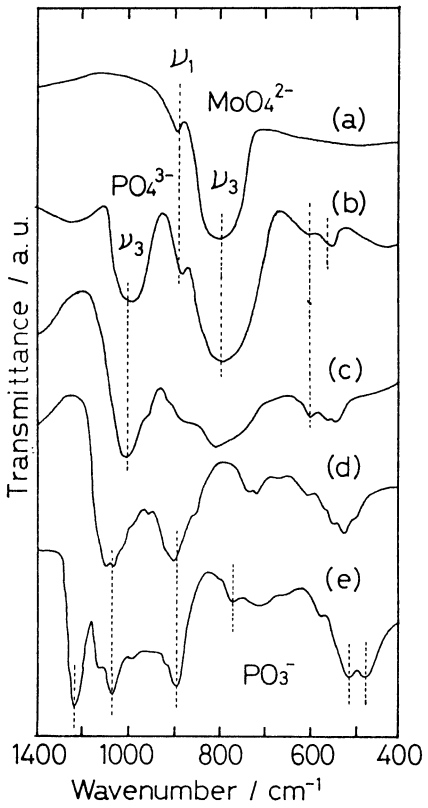

Fig. 2. FT-IR spectra of the glasses: (a) 60AgI•40Ag_2MoO_4; (b) 60AgI•30Ag_2MoO_4• 10$AgPO_3$; (c) 60AgI•20Ag_2MoO_4• 20$AgPO_3$; (d) 60AgI•10Ag_2MoO_4•30$AgPO_3$; (e) 60AgI• 40$AgPO_3$ (mol%).

are respectively assigned to the ν_{as} and the ν_s modes of PO_2^- units in meta-phosphate groups, which have chain or ring structure.[6] The absorption bands at 890 and 770 cm^{-1} are ascribed to the ν_{as} and ν_s modes of P-O-P stretching, and the bands at 510 and 470 cm^{-1} to $O=P-O^-$ units. These results suggest that the phosphate groups in the glass exist as the meta-phosphate anion form of linear chain or ring structure of PO_4 tetrahedra, as expected from the chemical composition.

The spectrum (b) is of the $60AgI \cdot 30Ag_2MoO_4 \cdot 10AgPO_3$ glass. In the spectrum, there are three absorption bands at 995, 600, and 550 cm^{-1}, in addition to the two absorption bands at 875 and 795 cm^{-1} ascribed to the ortho-molybdate anions, MoO_4^{2-}. The absorption bands at 995 and 550 cm^{-1} are ascribed to the ν_3 and ν_4 of the monomeric ortho-phosphate ions, PO_4^{3-}, and the absorption band at 600 cm^{-1} is assigned to the ν_{as} mode of Mo-O-Mo bands attributed to the formation of condensed ions of MoO_4 tetrahedra.

The absorption bands ascribed to monomeric ortho-phosphates ions, PO_4^{3-}, are

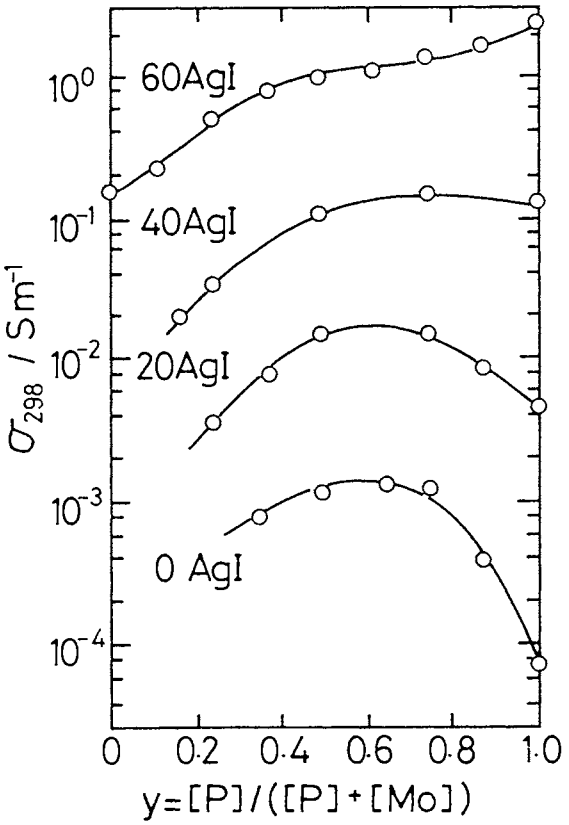

Fig. 3. Conductivities at 298 K, σ_{298}, of the glasses in the system AgI-Ag_2MoO_4-$AgPO_3$ as a function of the composition parameter y; y = [P] /([P] +[Mo]).

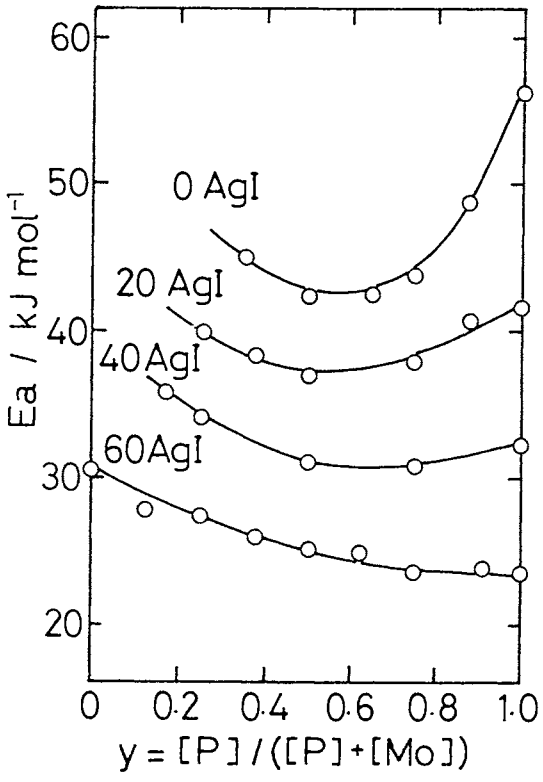

Fig. 4. Activation energies for conduction, Ea, of the glasses in the system AgI-Ag_2MoO_4-$AgPO_3$ as a function of the composition parameter y; y = [P] /([P] + [Mo]).

weakened and the absorption bands ascribed to condensed units of PO_4 tetrahedra are strengthened with an increase in the $AgPO_3$ content in the spectra (b) - (d).

Observation of the absorption bands resulting from such monomeric ortho-phosphate anions, PO_4^{3-}, and the condensed units of MoO_4 can be explained by the occurrence of the reaction $2\,MoO_4^{2-} + PO_3^{-} \longrightarrow Mo_2O_7^{2-} + PO_4^{3-}$ in the melt. The freezing of the melt through quenching causes the coexistence of these structural units in the glass. This result suggests that the frame work structure of oxoanions is changed by mixing two kinds of oxosalts, Ag_2MoO_4 and $AgPO_3$.

Figure 3 shows the composition dependence of ion conductivity at 298 K, σ_{298}, of the glasses in the system AgI-Ag_2MoO_4-$AgPO_3$; the abscissa of the figure is a composition parameter y, which denotes the ratio of the number of phosphorus atoms to the total number of phosphorus plus molybdenum atoms included in the glasses; $y = [P] / ([P] + [Mo])$. The conductivities for four series of glass compositions with a constant AgI content (60, 40, 20, and 0 mol%) are shown in the figure. At a given composition parameter y, the conductivity of these glasses increases with an increase in the AgI content. The conductivity of each series of glass composition with 60, 40, 20, and 0 mol% AgI shows the maximum in the deviation from additivity at around $y = 0.6$. The enhancement of conductivity diminishes with an increase in the AgI content. This behavior probably relates to the fact that the conductivity of the glasses is primary established by the AgI content and that the conductivity value itself is very high and the deviation from additivity becomes smaller.

The activation energies for ionic conduction, Ea, of the glasses in the system AgI-Ag_2MoO_4-$AgPO_3$ are plotted in Fig. 4 as a function of the composition parameter y. In the figure, Ea for four series of glass compositions with a constant AgI content (60, 40, 20, 0 mol%) is shown. The minimum in the deviation from additivity in Ea is also observed at around $y = 0.6$ in each series. The position of the minimum in Ea is nearly the same as that of the maximum in σ_{298} of the AgI-Ag_2MoO_4-$AgPO_3$ glasses.

These results indicate that the mixed anion effect in conductivity is closely related to the structural change of oxoanions included in the glasses.

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