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REVIEW

Development of New Glasses in the Solid State Ionics Field

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In recent years many new glasses have been developed which show very high ion conductivity. In the present paper these ion conductive glasses are reviewed from the points of view of (1) comparison of ion conductivity between glasses and crystals and the explanation of higher conductivity of glasses than crystals, (2) chemical compositions of new glasses, (3) conduction process, (4) mixed effect of ions on conductivity, (5) the application of hard and soft acids and bases theory to the development of high ion conducting glasses, and so on.

KEY WODRS: New Glass/ Solid State Ionics/ Conduction Mechanism/ Hard and Soft Acids and Bases Theory

1. INTRODUCTION

The electric conduction is divided into two categories; electronic and ionic conduction. The electronic conduction is, of course, the basis of "electronics" in modern age. The term "electronics" is used in science and technology where the movement of electrons (or positive holes) plays the key role in showing physical properties of semiconductor materials. The term was born with the invention of transistor which resulted in the change in the field of electron movement from gas (vacuum tube) to solid (transistor).

On the other hand the ionic conduction is usually observed in liquid electrolytes, since ions are very heavy and large in size compared with electrons and thus the movement of ions is usually very difficult in solids. The structural requirements are essential for ion movement in solids. Three types of such requirements are well known; (a) the introduction of lattice defects observed for example in stabilized zirconia, (b) the special structure like layered structure in β-Al_2O_3, and (c) the averaged structure in α-AgI.[1)]

These three types are, of course, in crystalline solids. We can expect that glasses show higher ion conductivities than crystals since they have random structure and thus much open space. This is the starting point for developing new glasses with high ion conductivities.

The fast ion conduction in solids including crystalline and glassy materials is the basis for solid state "ionics" where solid replaces liquid (electrolyte). We can expect the new era of ionics just like in "electronics" if we can develop excellent materials with high ion conductivities.

In this paper we review the process of developing new glasses with high ion conductivities

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and several features of these glasses, which are sometimes called "superionic conducting glasses," "superionic glasses," or "fast ion conducting glasses".[1-5]

2. COMPARISON OF ION CONDUCTIVITY BETWEEN GLASSES AND CRYSTALS

Figure 1 shows the comparison of conductivity at 25°C, σ_{25}, between glasses and crystals as a function of composition in the system AgI-Ag_2O-P_2O_5.[6] The σ_{25} values of glasses are higher by 1~2 orders of magnitude than those of crystallized samples in the whole range of glass formation. This fact is a striking contrast to the electronic conduction, in which electrons and holes are scattered by phonons and, thus, the lattice disorder increases the scattering of these charge carriers to bring the lower conductivity in glasses.

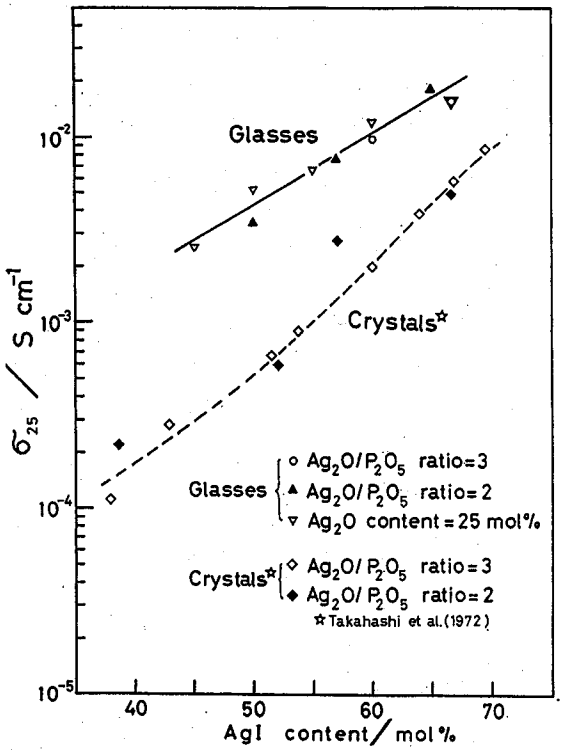

Fig. 1. Comparison of conductivity at 25°C, σ_{25}, between glasses and crystals in the system AgI-Ag_2O-P_2O_5.

Figure 2 shows another example of the merits of glass formation in the enhancement of ionic conduction.[1] This figure shows the temperature dependence of several Ag^+ ion conducting glasses, together with typical crystals marked by the symbol (c).

The high conductivity of glasses containing AgI is explained in relation to the high conductivity of α-AgI. Figure 2, however, shows that the glasses containing AgBr or AgCl, in which there is no conductive phase like α-AgI, exhibit high conductivities ; we consider such high conductivities of these glasses result from vitrification.

Besides their higher conductivities, glasses have several advantages such as isotropic

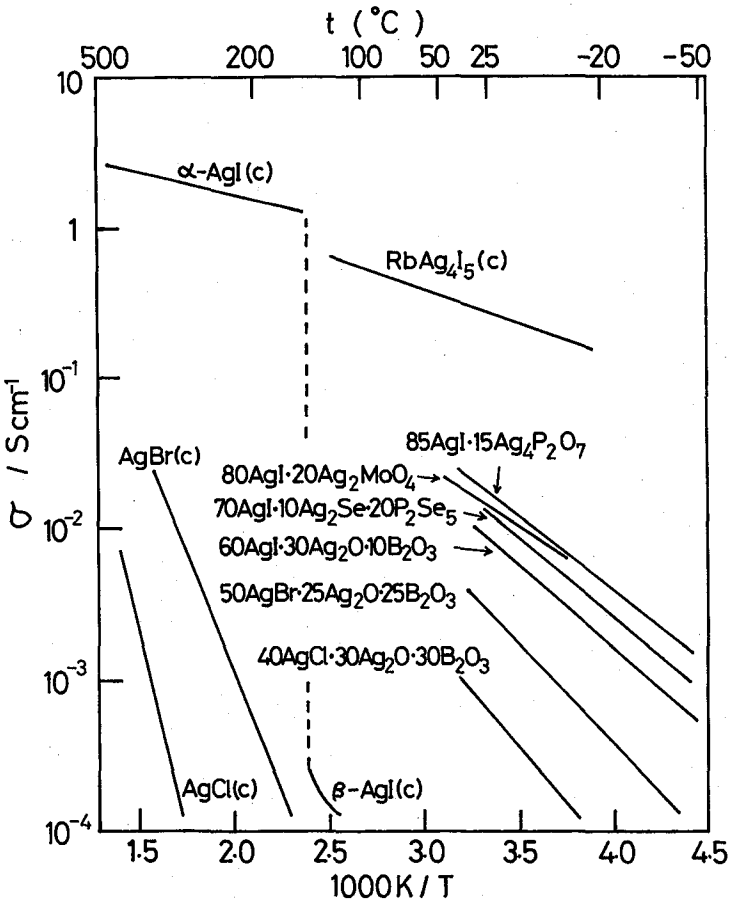

Fig. 2. Temperature dependence of conductivity of Ag^+ ion conducting glasses.

Table 1. Merits of vitrification.

1.	Higher conductivity
2.	Isotropic property
3.	No grain boundary
4.	Ease of shaping into various forms
5.	Ease of thin film formation
6.	Wide selection of glass-forming systems
7.	Wide range of control of properties with changing chemical compositions

properties, ease of thin film formation, and so on.[3,7] These merits are summarized in Table 1.

3. EXPLANATION OF HIGHER CONDUCTIVITY IN GLASS THAN IN CRYSTAL

At the time Fig. 2 was made, the achievement of higher conductivities in glasses than in crystals was simply thought to be due to the open structure with larger free space in glass,[1] and the proper explanation could not be given.

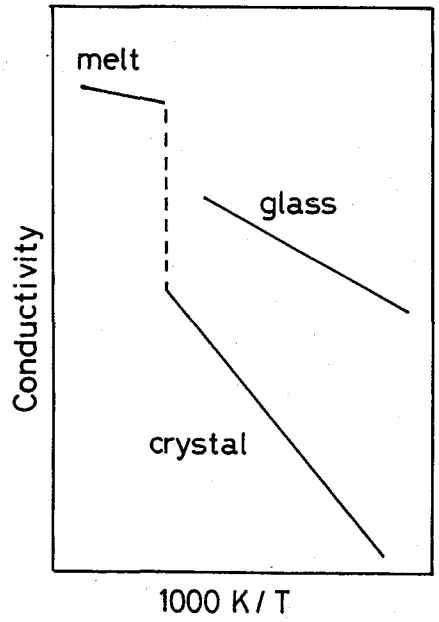

Fig. 3. Schematic representation for showing why glasses have higher conductivities than crystals do.

Now the reason why glasses show high conductivities even if the glasses contain no high conductivity phase is explained as follows by using a schematic illustration of Fig. 3.[5] The melt of a compound usually shows high conductivity and low activation energy for conduction. The conductivity drops at the transformation from the melt to the crystal and the crystal generally shows the low conductivity and the high activation energy for conduction. The glass must show the conductivity and activation energy in between those of the melt and the crystal, since the glass is prepared by quenching the melt, and structure of the melt is generally reserved to a great extent in the glass. The conductivity is, of course, a structure-sensitive property, and thus the conductivity of glass depends largely on the conductivity of the melt.

On the other hand the freezing of the structure takes place at temperatures close to the melting point (strictly speaking, at the fictive temperature). If the drop of the conductivity is small, we can expect a high conductivity in the glass. If the drop is large, the conductivity of the glass will become low. We can therefore conclude that a high melt conductivity and the small difference in conductivity between melt and crystal at the melting point are important factors for developing glasses with high conductivities.

4. DEVELOPMENT OF NEW GLASS-FORMING SYSTEMS WITH HIGH ION CONDUCTIVITY

In Fig. 4 the conductivities of several glasses symbolized by (g)[4,6,8~10] are compared with those[11] of melts symbolized by (l) and crystals symbolized by (c) of some halides of silver, copper, and alkalis.[5]

In the figure it is seen that the conductivities of melts of these halides do not change so much and the difference between melts and crystals is small in halides of silver and copper, but the

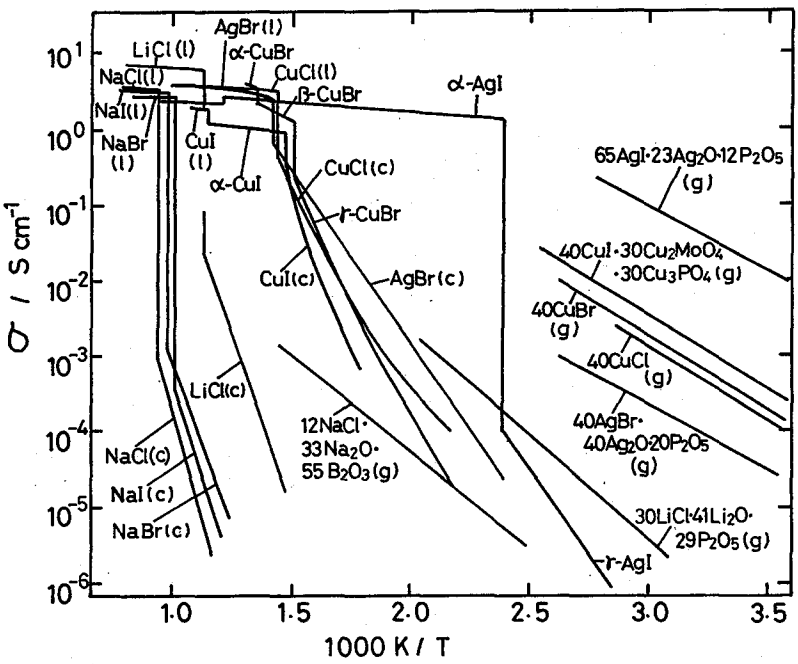

Fig. 4. Comparison of ion conductivities among several melts, crystals, and glasses of halides of silver, copper, and alkalis.

difference is large in alkali halides. We can thus expect that the high conductivity can be achieved in glasses containing halides of silver and copper while the high conductivity seems difficult to be achieved in glasses containing alkali halides. In fact the examples of glasses shown in the figure prove that the expectation above is valid.

In addition this figure shows the comparison of the effect of the difference in halide ions and metal ions on conductivity; in silver halide-containing glasses, the substitution of bromide for iodide decreases largely the conductivity while in cuprous halide-containing glasses the substitution of halide ions affects the conductivity only slightly. This is probably due to the large difference in conductivity at the melting point between AgI and AgBr and to the small difference among CuI, CuBr and CuCl.

Higher conductivities of LiCl-containing glasses than those of NaCl-containing glasses are probably caused by the smaller difference in conductivity of the melt and crystal of LiCl than NaCl.

From the context above it seems difficult to develop glasses showing very high alkali-ion conductivities via melts.

As an example showing the variety of glass formation in solid state ionics, Ag^+ ion conducting glasses are summarized in Fig. 5.[12] The compositions are first expressed in the form of AgI-Ag_2O-M_mO_n systems, where M_mO_n is a given oxide like B_2O_3, GeO_2, P_2O_5, MoO_3 as shown in Fig. 5. We have found these systems form new classes of highly conductive glasses. The development of these new glasses has started from the accidental finding of glass formation in the system AgI-Ag_2SeO_4 by Kunze.[13]

We have also found that the replacement of I and/or O with other elements in the same

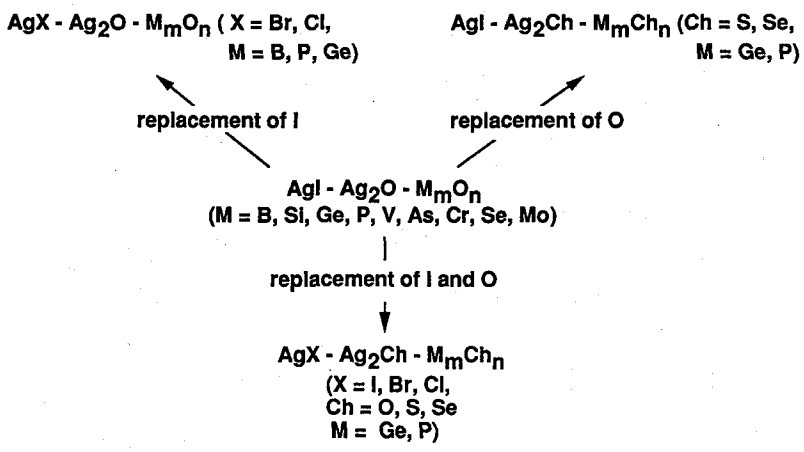

Fig. 5. Glass-forming systems with replacement of I and O in the systems AgI-Ag_2O-M_mO_n.

periodic group can form glasses ; the compositions of these glasses can be expressed as the systems AgX-Ag_2O-M_mO_n, AgI-Ag_2Ch-M_mCh_n, and AgX-Ag_2Ch-M_mCh_n, where X is a halide ion like I, Br, and Cl, and Ch is a chalcogenide ion like O, S, and Se.[1,12,14,15]

We have prepared new glasses more than 1,000 in these systems ; any glass showed high Ag^+ ion conductivities.

5. CONDUCTION PROCESS

Figure 6 shows an example of structure models of those new glasses ; in this figure the glasses in the system AgI-Ag_2MoO_4 (or AgI-Ag_2O-MoO_3) are chosen.[2,16]

Open circles denote Ag^+ ions, and the most important thing is that two types are illustrated among these Ag^+ ions ; circles with a black star and with a thin asterisk. The former is mainly surrounded by only I^- ions, and the latter by MoO_4^{2-} and I^- ions. The presence of strong partial covalency between Ag^+ ions marked by the asterisk and MoO_4^{2-} ions has been proved by

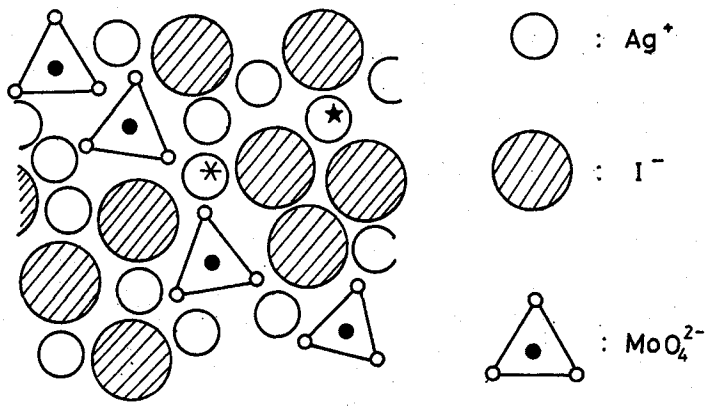

Fig. 6. A structure model explaining the conduction process in AgI-Ag_2MoO_4 glasses.

the band shift of the IR spectra.[17] Silver ions marked by the asterisk must be less mobile, because of such strong partial covalency, than the Ag^+ ions marked by the star. This means in turn that there are electrically two types of Ag^+ ions—less mobile and more mobile; this model is a schematic representation for the partial contribution of Ag^+ ions to the conduction.[1,18]

The conduction process mentioned above is explained in another way using a potential diagram shown in Fig. 7; the wide, shallow potential is formed by the interaction of Ag^+ ions with iodide ions, while the narrow, deep one is formed by the interaction of Ag^+ ions with oxide ions.[1] Considering the disordered structure of glass a random distribution of potential energy among the potentials formed only by the iodide or oxide ions must be present. However, the potential energy differences formed by the coexistence of iodide and oxide ions must be much larger than the width of the random distribution formed by each type of anions. The potential curves shown in the figure should be considered to involve the random distribution of potential energy formed by each anion

In the figure three types of combination are shown; (a) shallow-shallow (iodide-iodide), (b) shallow-deep (iodide-oxide), and (c) deep-deep (oxide-oxide). The Ag^+ ions trapped in the deep potential wells are less mobile than those in the shallow wells.

The carrier concentration must depend on how many Ag^+ ions are located in the shallow

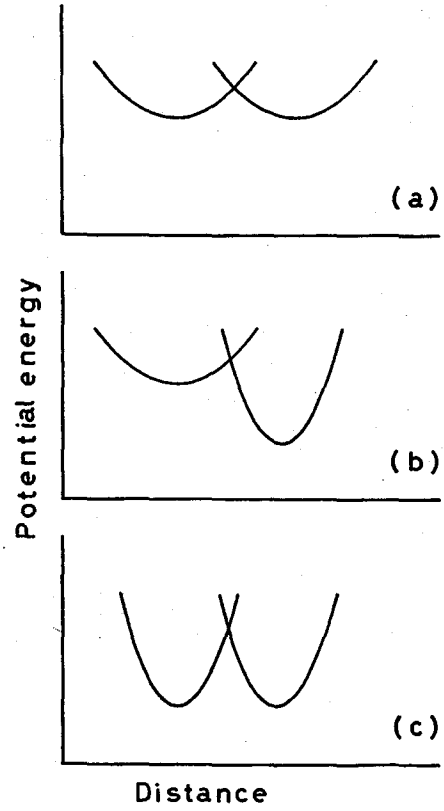

Fig. 7. Potential energy diagrams explaining the conduction process in superionic glasses (see text for details).

wells, and the mobility must depend on how long the shallow wells are connected like (a) in Fig. 7. When the shallow wells are connected for a long period, they form a path favorable for ion transport. We refer to such a path as the "diffusion path". We propose that high conductivities are mainly controlled by the presence and nature of the "diffusion path" in the glasses containing two different anions. We can thus call the transport process the "diffusion path model".[1,18,19] The diffusion path could be formed more easily in the disordered than in the ordered matrix, since the configurational freedom in the former is much higher than in the latter

The above model claims the presence of two types of Ag^+ ions, mobile and immobile ones; the former Ag^+ ions interact with iodide ions and are located in the potential wells like (a) in Fig. 7 and the latter ones interact with oxide ions and are located in the wells like (c).

It should additionally be remarked that potential wells connected like (b) in Fig. 7 must be present in those glasses due to their random structure; Ag^+ ions in the left (shallow wells) can jump to the adjacent site, but those in the right (deep wells) find it more difficult to jump. The Ag^+ ions located in the shallow wells in (b) must be observed as less mobile than those in the wells like (a) and much more mobile than those in the deep wells like (c). If there were only two types of wells like (a) and (c), the difference between mobile and immobile Ag^+ ions would be clear. However, the presence of the potential wells like (b) may make the difference obscure between mobile and immobile ions.

There are two other famous models on conduction process in glasses; the random site model[20,21] and the weak electrolyte model.[22,23] It is still controversial which model is the best one to explain the high conductivities in these glasses; also it is still not decisive whether two types of Ag^+ ions can experimentally be distinguishable or not, and whether the AgI-like microcluster as shown in Fig. 5 is present or not. Further detailed study is strongly needed.

6. MIXING EFFECT OF IONS ON CONDUCTIVITY: MIXED-ANION EFFECT

The mixed-alkali effect is well known in the field of ion conduction in glass; i.e. the minimum in composition dependence of conductivity is observed when two different types of alkalis are mixed in glass.

In contrast to the mixed-alkali effect, we have observed the enhancement or maximum in composition dependence of conductivity when two different types of anions are mixed.[4,24,25]

An example is shown in Fig. 8 for Ag^+ ion conducting glasses in the system AgI-Ag_2MoO_4-$AgPO_3$.[26] In this figure the conductivities at 298 K are plotted against the 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 primarily established by the AgI content and that the conductivity value itself is very high and the deviation from additivity becomes smaller.

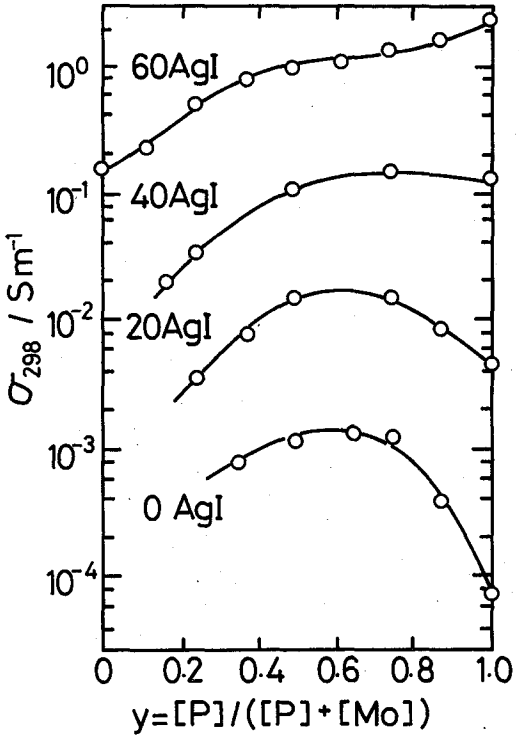

Fig. 8. Conductivities at 298 K, σ_{298}, of the glasses in the system AgI-Ag_2MoO_4-$AgPO_3$ as a function of the composition parameter y; y=[P]/([P]+[Mo]).

We have now known that there are two different types of variation in composition dependence of conductivity; the observation of maximum and minimum in cation conducting glasses.

Recently fluoride ion conducting glasses have been developed like ZrF_4-based glasses. In these anion conducting glasses, we can test the mixing effect of ions on conductivity. There are two types of mixing in anion conducting glasses; anion mixing and cation mixing. Then we have noticed that there are four-types of ion-mixing as shown in the first line of Table 2.[25] This

Table 2. Four types of cation-mixing and anion-mixing effects on ionic conductivity. M^+, N^+: cation, X^-, Y^- anion, ↓: decline, ↑: enhancement.

Mixed ions	Cation conduction		Anion conduction	
	cation	anion	cation	anion
ions present in glass	M^+, N^+ X^-	M^+ X^-, Y^-	M^+, N^+ X^-	M^+ X^-, Y^-
mobility	↓ ↑	↑ ↓	↓ ↑	↑ ↓
charge carrier	M^+, N^+	M^+	X^-	X^-, Y^-
conductivity	↓	↑	↑	↓
name	mixed -cation effect I	mixed -anion effect II	mixed -cation effect II	mixed -anion effect I

table summarizes the conductivity variations accompanying the ion mixing for each case; M^+ and N^+ indicate cations, X^- and Y^- indicate anions, and the upward and downward arrows denote the enhancement and decline, respectively (the length of the arrows qualitatively indicates the degree of enhancement or decline). This expectation comes from the following hypothesis proposed previously.[1)]

Mixed species (cations in cation mixing and anions in anion mixing) decline in diffusivity or mobility, and non-mixed species (anions in cation mixing and cations in anion mixing) are enhanced in transport. Since the mobility decline in the mixed species seems to be caused by the direct interaction between theses species, the mobility decline of the mixed species is predicted to be more remarkable than the mobility enhancement of the non-mixed species. The conductivity measurements in glass reflect the transport of more conductive species only (cations in cation conductors and anions in anion conductors), and thus the contrary tendency in conductivity variation accompanying the ion mixing is observed between the cation- and anion-conducting glasses.

The expectation demonstrated in Table 2 has been proved to be in good agreement with the experimental result.[25)]

The mixed-alkali effect only has long been known. According to Table 2, there are two types of mixed-cation effects and of mixed-anion effects. Thus, we propose to name each behavior for simplification as shown in the bottom line of Table 2: the "mixed-cation effect" is for the behavior observed with cation mixing and the "mixed-anion effect" for anion mixing. When the decline of conductivity is observed with the ion mixing, "I" is added to the name. When the enhancement is observed, "II" is added. Thus, we can simply rearrange the four types of conductivity variation accompanying the ion mixing as shown in the bottom line.[25)]

7. RELATION BETWEEN CONDUCTIVITY AND ELECTRONIC CONFIGURATION OF IONS

7.1. Development of Cu^+ Ion Conducting Glasses

When we compare the conductivity values of glasses with similar chemical compositions, we can usually find that the sequence of conductivity is:

$$\sigma(Ag^+) > \sigma(Li^+) > \sigma(Na^+) \tag{1}$$

where $\sigma(M^+)$ stands for the conductivity of the glasses containing M^+ ions. Some examples have been shown in Fig. 4, and much more clear example is shown in Table 3, where the conductivity of $40M_2S{\cdot}60GeS_2$ (mol%, M=Ag, Li, Na) is compared.[3,27)] With the ionic radius

Table 3. Comparison of conductivity at 25°C, σ_{25}, of $40M_2S{\cdot}60GeS_2$ (mol%) glasses together with several parameters.

Cations	σ_{25}/Sm^{-1}	Radii/pm	Configuration	Classification of Lewis Acids
Ag^+	1.5×10^{-2}	126	[Kr core]$4d^{10}$	Soft
Cu^+	?	96	[Ar core]$3d^{10}$	Soft
Li^+	4×10^{-4}	68	[He core]	Hard
Na^+	2×10^{-5}	97	[Ne core]	Hard

taken into account, the above sequence (1) can not easily be explained. The ionic radii of Ag^+, Cu^+, Li^+, and Na^+ are also listed in Table 3, together with the electronic configuration of these ions. The radius of Ag^+ ions is nearly twice as large as that of Li^+ ions. In spite of such ionic radius values, the conductivity sequence (1) above is well established.

On the other hand, Li^+ and Na^+ ions have the s^2 and s^2p^6 configuration (rare gas type) in the outermost orbitals, while Ag^+ ions have the complete d^{10} configuration, and thus Li^+ and Na^+ ions are classified as hard Lewis acids, but Ag^+ ions as a soft Lewis acid.[28] We have postulated that such a difference of electronic configuration of ions, as well as the radius, affects the ion transport, and therefore affects the conductivity of glasses.[1,4,29] Since Cu^+ ions have a similar d^{10} configuration and a smaller radius than that of Ag^+ ions, glasses containing Cu^+ ions may be expected to exhibit higher conductivities than those of glasses containing Ag^+ ions.

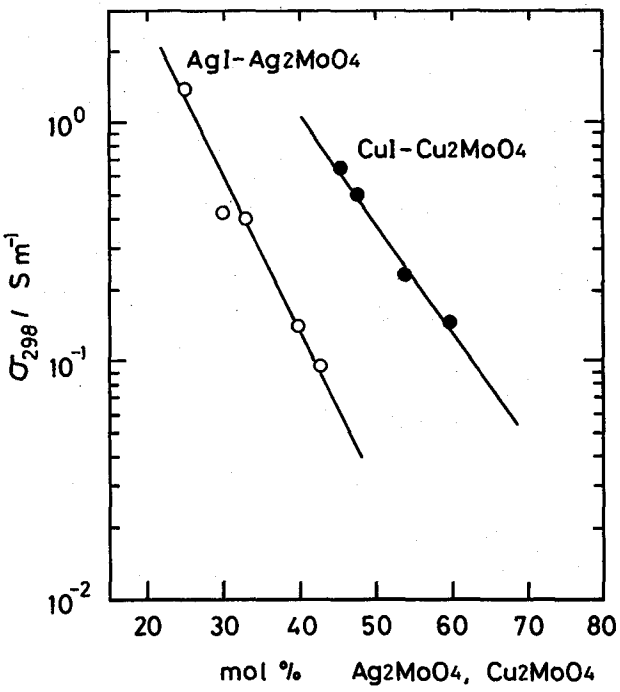

Fig. 9. Comparison of conductivities at 298 K, σ_{298}, of the glasses in the systems $CuI\text{-}Cu_2MoO_4$ and $AgI\text{-}Ag_2MoO_4$ as a function of the composition.

From the above consideration we can expect that Cu^+ ion containing glasses exhibit higher conductivities than those of Ag^+ ion containing glasses. Since the oxidation state of +1 for copper, i.e. Cu^+, is not so stable in glass, there have been very few papers on Cu^+ ion conducting glasses to date. Fortunately we have found several new glass-forming systems.[4,29,30] Among these, the conductivities of glasses in the system $CuI\text{-}Cu_2MoO_4$ at 298 K, σ_{298}, are shown in Fig. 9[29] as a function of composition and compared with those of glasses in the system $AgI\text{-}Ag_2MoO_4$.[31] The σ_{298} of glasses in the system $CuI\text{-}Cu_2MoO_4$ are 10 to 20 times larger than those of the glasses with the same iodide content in the system $AgI\text{-}Ag_2MoO_4$. In a strict sense, the comparison of conductivity of these two systems may have some problems, because the glass-

forming regions of the systems do not overlap.

7.2. Development of Li^+ Ion Conducting Glasses

The conductivities of glasses containing Cu^+ or Ag^+ ions are significantly higher than those of glasses containing Li^+ or Na^+ ions at room temperature as described already. Cu^+ and Ag^+ ions have the same complete d^{10} electronic configuration in the outermost orbitals, and thus Cu^+ and Ag^+ ions are classified as soft Lewis acids. In contrast, Li^+ and Na^+ ions are classified as hard Lewis acids, as mentioned above. Thus the big difference in conductivity must primarily result from the electronic configuration of the mobile ions. In addition, the higher conductivities of the Cu^+ glasses than those of Ag^+ glasses are of course caused by the smaller ionic radius of Cu^+ ions than that of Ag^+ ions of the same electronic configuration.

In the preceding section the combination of soft acids with hard bases has been proved to be important to obtain highly conductive glasses.

The most favorable ion species we want to develop is Li^+ ions, which are unfortunately a hard acid. If we extend the consideration mentioned in the preceding section for the development of Li^+ ion conducting glasses, one way is to change the glass matrix composition from oxides to sulfides; sulfide ions are classified as a "soft base."

An example of conductivities of the Li_2S-SiS_2 based glasses is shown in Fig. 10.[32] In this figure the doping of Li_3PO_4 to the base glass $0.6Li_2S{\cdot}0.4SiS_2$ (mole ratio) is tried. The conductivity of the base glass is in the order of 10^{-4} Scm^{-1} at room temperature, which can be compared with the conductivity of 10^{-6} Scm^{-1} for $0.6Li_2O{\cdot}0.4SiO_2$. The increase by two orders of magnitude could be attributed to the change of oxide to sulfide, i.e. the hard to soft base of the glass matrix.

The addition of a small amount of Li_3PO_4 enhances the conductivity; this enhancement of

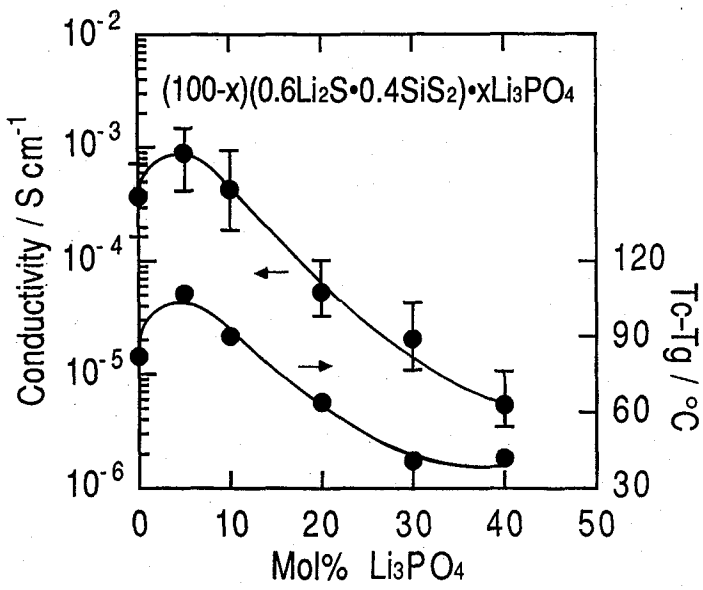

Fig. 10. Composition dependence of conductivity at 25°C for the $(100-x)(0.6Li_2S{\cdot}0.4SiS_2){\cdot}xLi_3PO_4$ glasses. The difference between crystallization and glass transition temperatures is also shown.

conductivity with the addition of oxosalt to sulfide based glasses might be due to the mixed-anion effect II mentioned in section 6. The Li^+ ion conductivity of about 10^{-3} Scm^{-1} at room temperature gives strong hope for practical applications in electrochemical devices.

In this figure the composition dependence of (Tc-Tg) is also shown; the temperature difference between crystallization Tc and glass transition Tg is a measure of thermal stability. It is noticeable that the thermal stability increases with the addition of a small amount of Li_3PO_4 as well as the increase in conductivity.

As mentioned above, Li^+ ion conducting glasses become hopeful for practical applications in near future.

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