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REVIEW

Solid silver ion conductors[*]

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Materials exhibiting high ionic mobilities in the solid state at room temperature have mainly been found in the silver ion conductors which are based on silver iodide. Though silver iodide is a low conductivity solid at room temperature, it exhibits high ionic conductivity at relatively higher temperatures. In order to stabilize this high conductivity phase of silver iodide at room temperature, the introduction of foreign cations or anions into the lattice of silver iodide has been attempted. In this paper, the various silver ion high conductivity solids are reviewed, together with those showing both high ionic and electronic conductivity.

1. Introduction

In recent years solid state devices have been much in demand from various points of view. But, till quite recently, it has been difficult to use electrolytes in the solid state over a wide temperature range.

In our laboratory, investigations to search for solid electrolytes which exhibit high ionic conductivity at room temperature were begun about ten years ago with the object of using the electrolyte in the solid state at ambient temperature. Since then, various high ionic conductivity solids have been discovered at room temperature as well as at high temperature.

For the present, the most important conductor which exhibits high ionic conductivity at room temperature in the solid state is the silver ion conductor.

In this paper, the solid silver ion conductors are reviewed.

2. Silver ion conductors based on silver iodide

Up to the present, a large number of silver ion conductors based on silver iodide have been reported [1–7]. Silver iodide is generally a mixture of the β- and the γ-phases [8, 9] and has a low conductivity below 146°C. At 146°C, it transforms to the α-phase [10–16] and, above this temperature, its conductivity increases suddenly to about 10^0 $(\Omega\ \mathrm{cm})^{-1}$ which is five to six orders of magnitude greater than that at 100°C to room temperature [17]. The charge carrier in silver iodide has been shown to be the silver ion [18]. Silver iodide in the β phase shows a hexagonal close packing of the iodide ions and, in the α-phase, a body-centered cubic structure with iodide ions with two AgI entities in a unit cell. These two silver ions in a unit cell have been recognized to be distributed statistically over 42 available sites; in this respect it may be considered as an 'average structure' [10, 19].

That is to say, one can consider that even at room temperature the material having an average structure of this kind may show high ionic conductivity in the solid state; it allows one, in any case, to connect ionic conductivity with crystal structure for studies on high ionic conductivity solids. That is, in order to obtain high silver ion conductivity solids at room temperature, one may search for a material which has an average structure like α-silver iodide at room temperature. It may be possible to stabilize the average structure like α-silver iodide at lower temperatures by introducing stabilizer ions into its lattice thus hindering the formation of close packing of the iodide ions which may be a cause of the low ionic con-

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duction in β-silver iodide. As stabilizer ions, one may select three groups, namely anions or cations or both. At the time of introducing these ions into the lattice of silver iodide, they must be in the form of salts and when these salts are simple inorganic salts, one would like them to have the possibility of assuming a cubic crystal structure which will in turn induce silver iodide to assume a cubic crystal structure like α-silver iodide at room temperature.

2.1. *Anions*

2.1.1. *Sulfide ion.* The first success in finding a high ionic conductivity solid at room temperature was achieved by introducing the sulfide ion into the lattice of silver iodide [20–22]. Silver sulfide has a cubic structure α-phase above 175°C which is a high temperature modification. If one makes silver iodide react with silver sulfide at relatively high temperature in 1 : 1 molar ratio, a compound Ag_3SI is obtained which shows a high silver ion conductivity of 0·01 $(\Omega\ cm)^{-1}$ at 25°C [21]. Ag_3SI transforms from the β- to the α-phase at 255°C and β-Ag_3SI which is stable at lower temperatures has a simple cubic structure with the lattice constant of 4·91 Å [20]. There is one Ag_3SI in a unit cell, and three silver ions in a unit cell have been recognized to be distributed statistically over 12 available interstitial sites in the {100} plane of the cube, thus forming an average structure.

Electronic conductivity in Ag_3SI appears with deviation from the stoichiometric composition, and Ag_3SI which exhibits low electronic conductivity must be synthesized by heating silver iodide and silver sulfide under an appropriate vapor pressure of sulfur thus hindering the vaporization of sulfur at the synthesizing temperature. In Fig. 1, the electronic conductivity of Ag_3SI is shown when synthesized by heating a mixture of silver iodide and silver sulfide at 550°C for 17 h under a sulfur pressure of one atmosphere. The electronic conductivity is evaluated [23] as 10^{-8} $(\Omega\ cm)^{-1}$ at room temperature [21]. Thus, Ag_3SI is a good silver ion conductor at room temperature except for its disadvantage in being decomposed by iodine with a resulting decrease in its conductivity [24]. In Fig. 2 the conductivity of Ag_3SI is shown against the reciprocal of the absolute temperature taking sulfur vapor pressure at the temperature of the synthesis of the Ag_3SI (550°C) as a parameter.

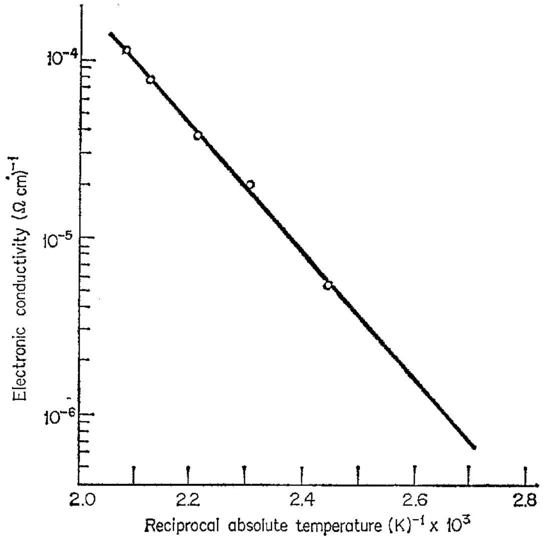

Fig. 1. Temperature dependence of the electronic conductivity of Ag_3SI in equilibrium with pure silver.

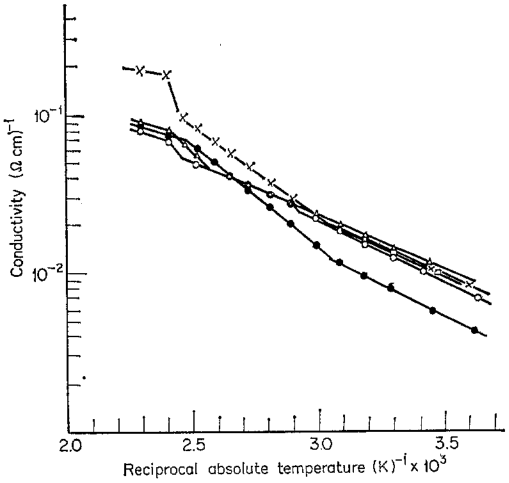

Fig. 2. Conductivities of Ag_3SI synthesized under various vapor pressures of sulfur. ○ Vapor pressure of sulfur 0·58 mm Hg; △ Vapor pressure of sulfur 100 mm Hg; □ Vapor pressures of sulfur 1 atm; × Vapor pressure of sulfur 2 atm; ● Vapor pressure of sulfur 3 atm.

Stimulated by this success, oxyacid ions have been introduced into the lattice of silver iodide in an attempt to obtain high silver ion conductivity solids at room temperature. Of the oxyacid ions introduced, the sulfate, orthophosphate, pyrophosphate and tungstate ions have been found to be effective in giving high ionic conductivity to silver iodide at room temperature.

2.1.2. *Sulfate ion* [25]. In this case, in other words in the silver iodide and silver sulfate system, a solid solution of α-AgI with Ag_2SO_4 is obtained by heating a mixture of 78 mole % AgI and 22 mole % Ag_2SO_4 which is found to have a high silver ion conductivity at -20°C. Though this solid solution decomposes to β-AgI and Ag_2SO_4 below 119°C as indicated in Fig. 3, if it is quenched to -20°C from 400°C (the reaction temperature of this solid solution), its conductivity has been found to keep a constant value of 0·02 $(\Omega\ cm)^{-1}$ at -20°C for at least one year. At room temperature, however, its conductivity decreases gradually with time which indicates that this solid solution may be frozen in at -20°C keeping the average structure.

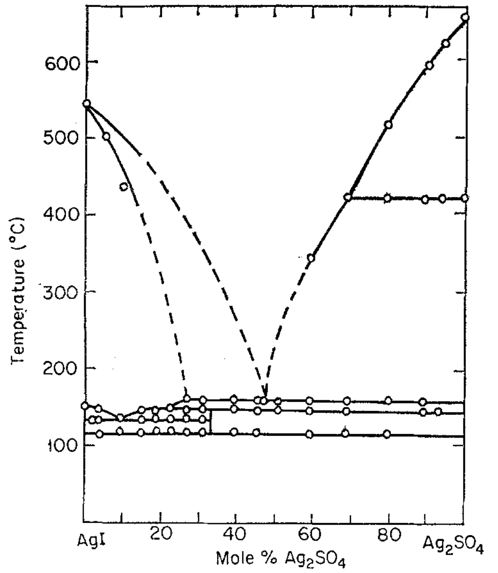

Fig. 3. Phase diagram of the system AgI-Ag_2SO_4.

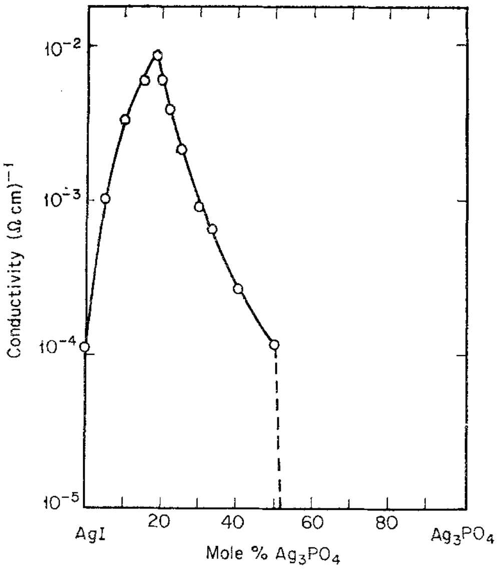

Fig. 4. Electrical conductivity of the system AgI-Ag_3PO_4 at room temperature.

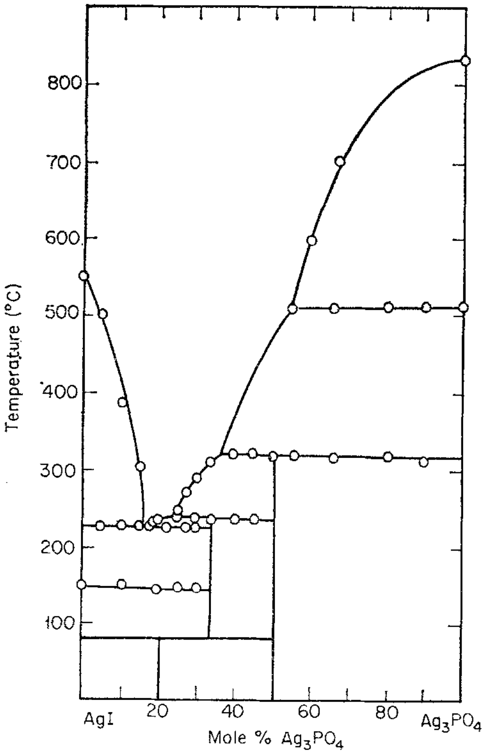

Fig. 5. Phase diagram of the system AgI-Ag_3PO_4.

2.1.3. *Orthophosphate ion* [26]. When silver iodide is made to react with silver orthophosphate at 200°–400°C for 18 h, a high ionic conductivity solid is obtained at the composition of 20 mole % Ag_3PO_4 as shown in Fig. 4. The phase diagram of the AgI-Ag_3PO_4 system is shown in Fig. 5. The high ionic conductivity solid obtained is found to correspond to a compound $Ag_7I_4PO_4$ which is orange colored and somewhat sensitive to light. The activation energy for silver ion conduction is 3·8 kcal $mole^{-1}$, the low value of which will suggest that this compound has an average structure. This compound has been found to have a simple cubic structure with the lattice constant of 10·6 Å.

2.1.4. *Pyrophosphate ion* [26.] Fig. 6 shows the phase diagram of the silver iodide and silver pyrophosphate system. Of the three compounds which are seen to exist at room temperature, $Ag_{19}I_{15}P_2O_7$ has been confirmed to have the highest conductivity at room temperature as indicated in Fig. 7. This compound is yellow colored with a little sensitivity to light. The activation energy for silver ion conduction in this compound is 3·3 kcal $mole^{-1}$ suggesting that $Ag_{19}I_{15}P_2O_7$ may again have an average structure. It has been found that this compound has a simple cubic structure with the lattice parameter of 11·2 Å.

2.1.5. *Tungstate ion* [27]. In Fig. 8, the conductivities of the reaction products between

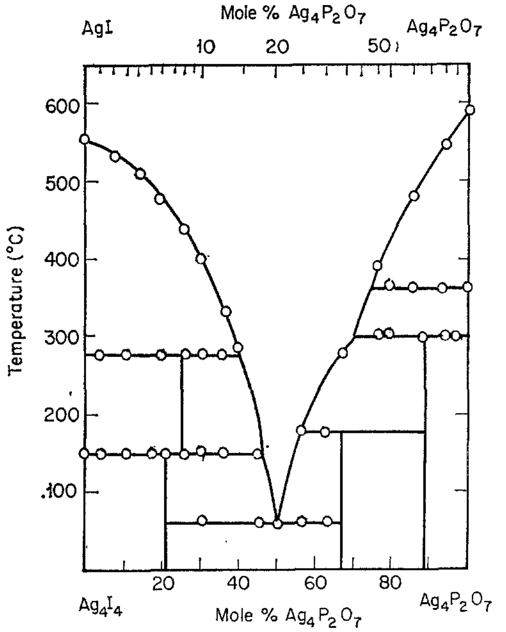

Fig. 6. Phase diagram of the system $AgI-Ag_4P_2O_7$.

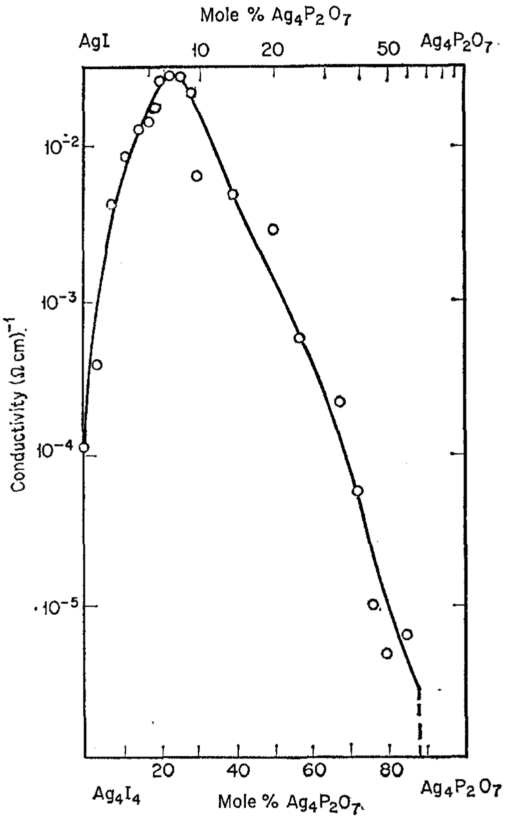

Fig. 7. Electrical conductivity of the system $AgI-Ag_4P_2O_7$ at room temperature.

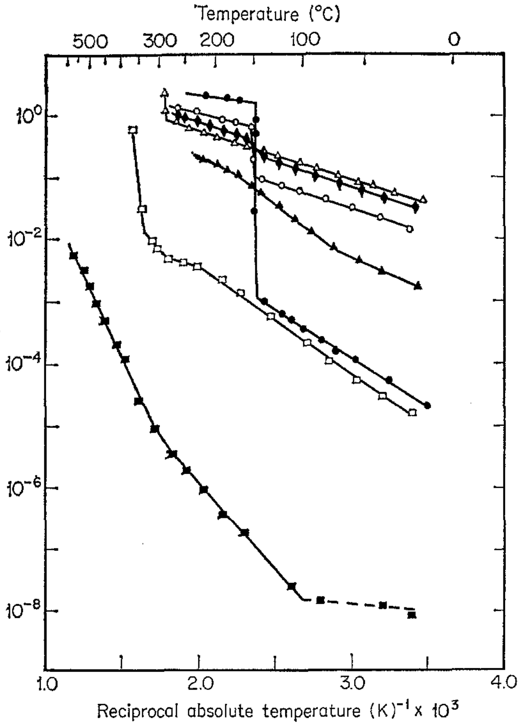

Fig. 8. Electrical conductivities of the system $AgI-Ag_2WO_4$ at various compositions. ● Ag_2WO_4 0 mole%; ○ Ag_2WO_4 10 mole%; △ Ag_2WO_4 20 mole%; ◆ Ag_2WO_4 30 mole%; ▲ Ag_2WO_4 40 mole%; □ Ag_2WO_4 66·7 mole%; ■ Ag_2WO_4 100 mole%.

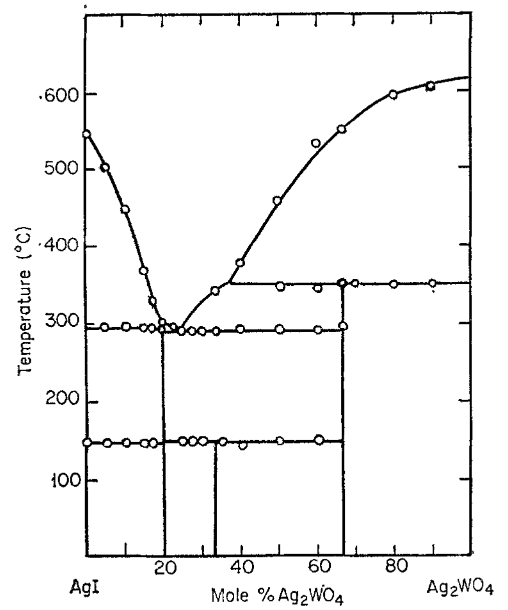

Fig. 9. Phase diagram of the system AgI-Ag_2WO_4.

silver iodide and silver tungstate are shown, the reaction temperature being 400°C. The highest silver ion conductivity at room temperature is found in the sample containing 20 mole % silver tungstate in silver iodide which corresponds to $Ag_6I_4WO_4$ as illustrated in the phase diagram shown in Fig. 9. The conductivity of $Ag_6I_4WO_4$ is 0·047 $(\Omega\ cm)^{-1}$ at 25°C with an activation energy of 3·6 kcal $mole^{-1}$ suggestive of an average structure.

In general, these high silver ion conductivity solids in the silver iodide and silver oxyacid salts systems are thermally stable and do not react with iodine or water vapour, thus keeping their conductivities constant in moisture as well as in iodine atmospheres. These properties are excellent characteristics when they are used practically.

2.2. *Cations*

The cations which are effective in giving high silver ion conductivity solids at room temperature when introduced into the lattice of silver iodide have been found to be the alkali metal and ammonium ions and the substituted ammonium ions.

2.2.1. *Alkali metal ion.* The introduction of the potassium and rubidium ions into the lattice of silver iodide has been found to be effective in creating a high silver ion conductivity solid at room temperature. The most well-known example of this group is $RbAg_4I_5$ [28–31]. $RbAg_4I_5$ is prepared by fusing a mixture of four moles of AgI and one mole of RbI *in vacuo* at 500°C before cooling abruptly to room temperature and annealing afterwards at 165°C for approximately 10 h. The conductivities of this group are shown in Fig 10. These values are the highest ionic conductivities ever measured in the solid state. The electronic conductivity of $RbAg_4I_5$ has been found to be 10^{-9} $(\Omega\ cm)^{-1}$ at room temperature. The activation energy of $RbAg_4I_5$ for silver ion conduction is as low as 1·7 kcal $mole^{-1}$ suggesting that $RbAg_4I_5$ will have an average structure. Actually, $RbAg_4I_5$ has been found to have a simple cubic structure, the lattice constant of which is 11·2 Å, thus having an open structure of the iodide ions. The crystal has diffraction symmetry of m 3 m and there are four $RbAg_4I_5$ in a unit cell, 16 silver ions being distributed statistically over 72 available interstitial sites of 4 (b), 8 (c), 12 (d) and two sets of 24 (e) [32]. Another distribution of the silver ions in a unit cell, however, has been reported; this states that there are three sets of crystallographically non-equivalent sites for the silver ions, one 8-fold set and two 24-fold sites, making a total of 56 sites for 16 silver ions per unit cell. The silver ions are not distributed at

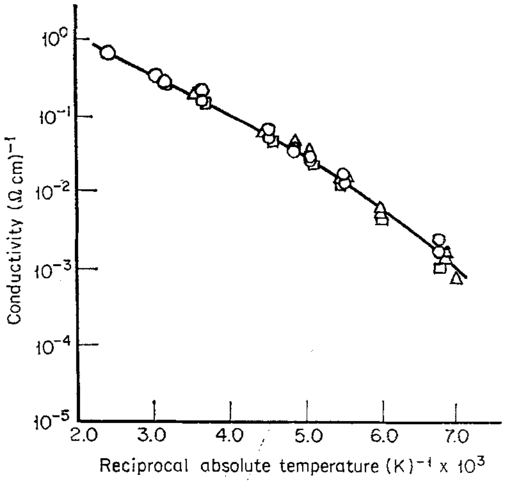

Fig. 10. Electrical conductivities of MAg_4I_5. ○ $RbAg_4I_5$; △ KAg_4I_5; □ $(K_3Rb)_{0\cdot25}Ag_4I_5$.

random over these sites, but there are, on average, 0·88±0·30 silver ions in the 8 (c) sites and 9·38±0·87 and 5·50±0·83 silver ions in the two sets of 24 (e) sites, respectively [33]. In either case, it probably is fair to say that $RbAg_4I_5$ has an average structure.

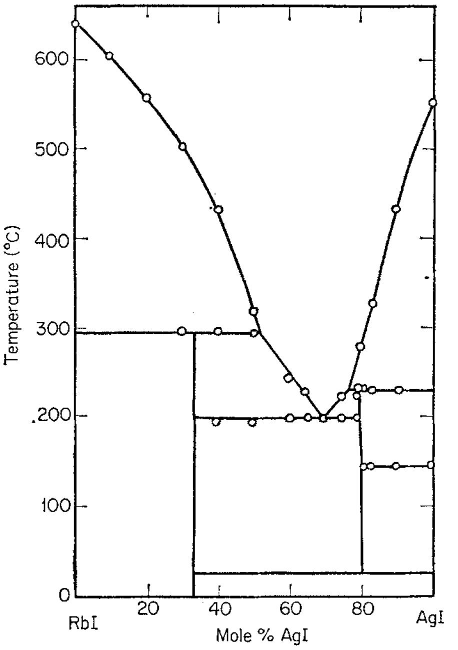

Fig. 11. Phase diagram of the system AgI-RbI.

Thermodynamically, $RbAg_4I_5$ is unstable below 27°C, decomposing to AgI and Rb_2AgI_3, both of which exhibit low conductivity [34]. In Fig. 11, the phase diagram of the AgI and RbI system is shown [6, 28]. The conductivity of $RbAg_4I_5$, however, is relatively high at lower temperatures as illustrated in Fig. 10 which implies that the activation energy for decomposition of $RbAg_4I_5$ is so large that $RbAg_4I_5$ remains frozen and continues to exhibit high conductivity at temperatures lower than 27°C. But, if $RbAg_4I_5$ is put in moisture or iodine atmospheres, its resistivity increases gradually at room temperature. In Fig. 12, the time dependence of the resistivity of $RbAg_4I_5$ in contact with iodine is shown in comparison with that of silver iodide containing oxyacid ions [26, 35]. Thus, it is difficult to obtain a highly stable solid state battery using $RbAg_4I_5$ as the electrolyte and iodine as the cathode material. Nevertheless, $RbAg_4I_5$ has the advantage of being able to be vacuum deposited to form a thin film [36].

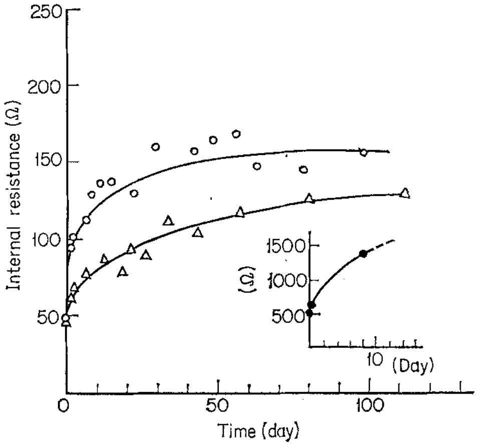

Fig. 12. Changes of the internal resistances of three cells at room temperature. ○ Graphite|$Ag_7I_4PO_4+I_2$|Graphite; △ Graphite|$Ag_{19}I_{15}P_2O_7+I_2$|Graphite; ● Graphite|$RbAg_4I_5+I_2$|Graphite.

2.2.2. *Ammonium and substituted ammonium ion* [28, 37, 38]. Introducing ammonium ions into the lattice of silver iodide has been found to lead to the formation of a compound which exhibits a high silver ion conductivity at room temperature [6]. Further, ammonium ions, in which hydrogen atoms have been substituted by organic radicals have been effectively introduced into the lattice of silver iodide to obtain a high ionic conductivity solid at room temperature. In Fig. 13, the composition dependence of the conductivity of the silver iodide and alkylammonium iodide systems is shown. As indicated clearly in the figure, the highest conductivity is given by the composition of one mole alkylammonium iodide and six moles silver iodide, that is C_nH_mNI 6AgI. These high conductivity solids are silver ion conductors in which the electronic conductivity is in the order of 10^{-10} $(\Omega\ cm)^{-1}$ at room temperature.

The crystal structure of $[(CH_3)_4N]_2\ Ag_{13}I_{15}$, which is composed of one mole tetramethylammonium iodide and 6·5 moles silver iodide, has been made clear [39]. In this compound, a hexagonal unit cell contains three $[(CH_3)_4N]_2\ Ag_{13}I_{15}$ and there are eight crystallographically non-equivalent sets of sites for the silver ions, that is, six 18-fold sets, one 6-fold set and one

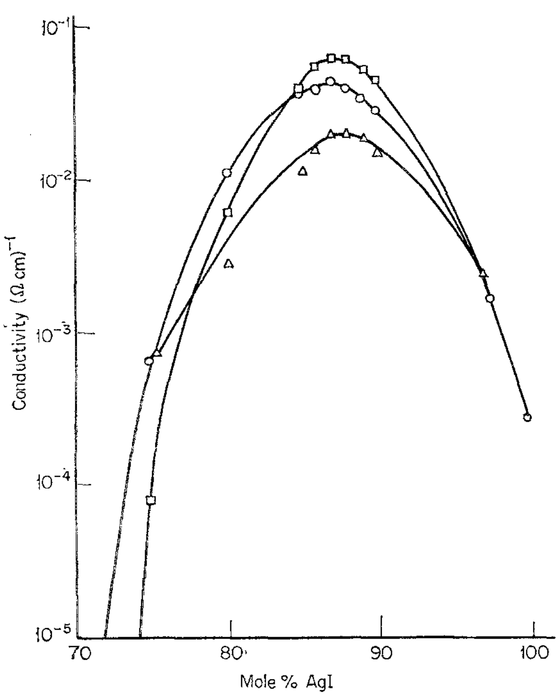

Fig. 13. Conductivities of the system substituted ammonium iodide-AgI at 22°C. ○ $(CH_3)_4NI$-AgI; □ $(CH_3)_2(C_2H_5)_2NI$-AgI; △ $(C_2H_5)_4NI$-AgI.

9-fold set. Thus, 39 silver ions are distributed, though non-randomly, over 123 tetrahedral sites.

It is striking progress in the study of solid silver ion conductors to find that ammonium ions substituted with organic radicals can be effectively introduced into the lattice of silver iodide to give a high ionic conductivity solid at room temperature.

A similar success has been achieved by introducing saturated azacyclic substituted ammonium ions e.g. the pyrrolidinium, piperidinium and quinuclidinium ions and their derivatives, and unsaturated azacyclic substituted ammonium ions such as the pyridinium and quinolinium ions and their derivatives into the lattice of silver iodide. Their conductivities are summarized in Table 1. The crystal structure of one of these high conductivity solids, pyridinium hexa-iodopenta-argentate $(C_5H_5NH)\ Ag_5I_6$, has been determined [40]. There are two $(C_5H_5NH)\ Ag_5I_6$ per hexagonal unit cell. The arrangement of the iodide ions is such that there are two sets of tetrahedra, 24 (m) and 6 (f), and one set of octahedra, 4(c), in the unit cell. The site occupancy of the silver ions is 4% of the (m) sites, 91% of the (f) sites and 89% of (c) sites at 23°C. There are straight channels parallel to the C-axis, that is [001], in this compound which may give a different mechanism of silver ion conduction from that in $[(CH_3)_4N]_2\ Ag_{13}I_{15}$. In any case, it has been pointed out that it is necessary to use substituted ammonium salts with molecular weights below 290g mole^{-1} to obtain satisfactory results [38].

Similarly, high silver ion conductivity solids have been obtained by introducing the polymethonium ions [41] and alkylalkylene amine ions [42] in to the lattice of silver iodide. They are represented by the formulae $C_nH_mN_2I_2$ 12 AgI, $C_nH_mN_3I_3$ 22 AgI and $C_nH_mN_4I \cdot 5AgI$, respectively and the values of their conductivities are listed in Table 1.

It may be expected that new compounds which exhibit high silver ion conductivity at room temperature will be found by introducing various organic ions into the lattice of silver iodide.

2.3. *Cations and anions*

2.3.1. *Mercuric ion and chalcogenide ion.* High conductivity silver ion conductors have been obtained by introducing the mercuric ion and

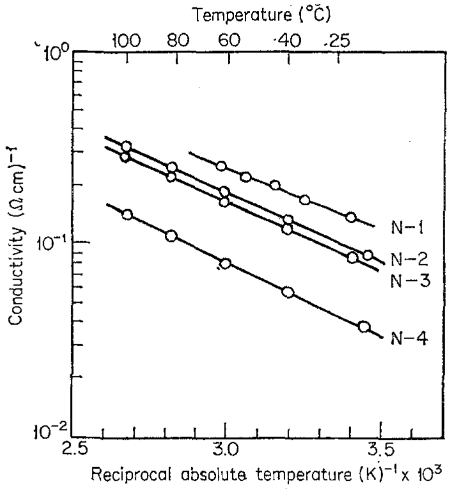

Fig. 14. Conductivities of the system AgI-Ag_2-Chal. HgI_2. N-1: $Ag_{2.0}Hg_{0.25}S_{0.5}I_{1.5}$; N-2: $Ag_{1.85}Hg_{0.40}Te_{0.56}I_{1.35}$; N-3: $Ag_{1.80}Hg_{0.45}Se_{0.70}I_{1.30}$; N-4: $Ag_{2.0}Hg_{0.5}/Se_{1.0}I_{1.0}$.

chalcogenide ions such as the sulfide, selenide and telluride ions into the lattice of silver iodide [42–47]. The highest conductivity solids have the compositions shown in Table 1. These solid electrolytes are the compounds having the body-centered cubic structures. In these compounds, an α-silver iodide type crystal structure has been found only in the sulfide ion containing compound which has 2·25 silver ions distributed statistically over 42 available sites. The crystals of the other compounds have diffraction symmetry of m 3 m and the available sites in a unit cell are not 42 but 30, that is 6 (b) and 24 (h). This difference in the number of available sites for the silver ion may be caused by the difference of the size of the chalcogenide ions. The mercuric ions do not contribute to the conductance. In Fig. 14, their silver ion conductivities are shown against the reciprocal of the absolute temperature.

2.3.2. *Alkali metal ion and cyanide ion.* The potassium or rubidium ion and the cyanide ion have been found to be effective in giving high silver ion conduction to the resulting solids [48, 49]. In Fig. 15, the conductivity of samples in the potassium cyanide and silver iodide system is shown against the content of potassium cyanide. The highest conductivity is obtained in the composition 4 AgI.KCN with an activation

Table 1. *Conductivities of the high silver ion conductivity solids at room temperature*

Substance		*Conductivity* $(\Omega cm)^{-1}$	*Temperature* °*C*
Ag_3SI		0·01	25
$Ag_5I_3SO_4$		0·02	−20
$Ag_7I_4PO_4$		0·019	25
$Ag_{19}I_{15}P_2O_7$		0·09	25
$Ag_6I_4WO_4$		0·047	25
$RbAg_4I_5$		0·27	24
KAg_4I_5		0·21	20
$NH_4Ag_4I_5$		0·19	20
$K_{0\cdot5}Rb_{0\cdot5}Ag_4I_5$		0·19	20
$K_{0\cdot5}(NH_4)_{0\cdot5}Ag_4I_5$		0·22	20
$Rb_{0\cdot5}(NH_4)_{0\cdot5}Ag_4I_5$		0·22	20
$K_{0\cdot33}Rb_{0\cdot33}(NH_4)_{0\cdot33}Ag_4I_5$		0·21	20
QAg_6I_7 ($C_nH_mNI\cdot6AgI$)			
Q = Tetramethyl ammonium		0·04	22
= Ethyltrimethyl ammonium		0·04	22
= Diethyldimethyl ammonium		0·06	22
= Trimethylisopropyl ammonium		0·04	22
= Trimethylpropyl ammonium		0·03	22
= Triethylmethyl ammonium		0·03	22
= Tetraethyl ammonium		0·01	22
QAg_xI_{x+1} ($C_nH_mNI\cdot xAgI$)			
Q = Piperidinium	$(x = 8)$	0·02	22
= 1,1-dimethylpyrrolidinium	$(x = 7)$	0·06	22
= Quinuclidinium	$(x = 6\cdot7)$	0·06	22
= 1,1-dimethylpiperidinium	$(x = 8)$	0·06	22
= *N*-methylquinuclidinium	$(x = 6\cdot7)$	0·05	22
= 5-azoniaspiro[4·4]nonane	$(x = 6\cdot7)$	0·02	22
= Pyridinium	$(x = 8)$	0·04	22
= 3-methylpyridinium	$(x = 6\cdot7)$	0·04	22
= 1-methylpyridinium	$(x = 6)$	0·01	22
= 1,3-dimethylpyridinium	$(x = 6\cdot7)$	0·03	22
= 3,5-dimethylpyridinium	$(x = 6\cdot7)$	0·02	22
= 1,2,6-trimethylpyridinium	$(x = 6\cdot7)$	0·02	22
= 1,2,4,6-tetramethylpyridinium	$(x = 6\cdot7)$	0·03	22
= 1-methylquinolinium	$(x = 4)$	0·02	22

(*continued*)

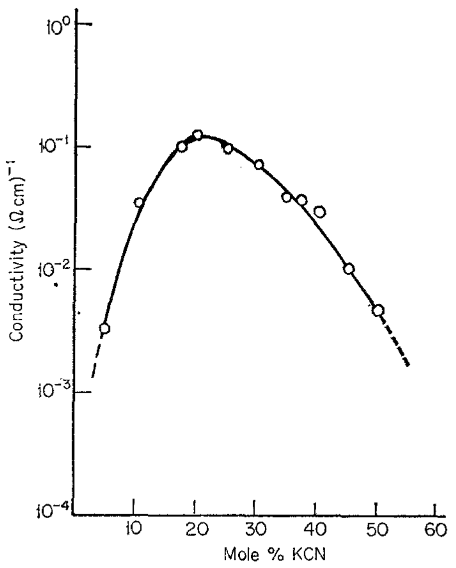

Fig. 15. Conductivity as a function of composition for the KCN-AgI system at 25°C.

energy for conduction of 1·94 kcal mole^{-1}. 4 AgI.RbCN and 8 AgI.KCN RbCN have also been found to have high silver ion conductivity. Of these compounds, rubidium containing ones have been recognized to be more stable than those containing potassium in moisture.

3. Silver ion conductors of the beta alumina type

A silver ion conductor has been found in the so-called beta alumina type compound [50, 51]. Beta alumina has a composition shown by the formula $Na_20.11Al_2O_3$ and by substituting for sodium in this compound with silver, silver beta alumina is obtained. This compound has a chemical formula of $Ag_{1+x}Al_{11}O_{17}$ (where $x = 0{\cdot}158 \pm 0{\cdot}004$) which indicates that it is a highly defective non-stoichiometric compound. Silver beta alumina is made up of close-packed

Table 1 *cont.*

Substance	*Conductivity* $(\Omega cm)^{-1}$	*Temperature* °*C*
$QAg_{12}I_{14}$ $(C_nH_mN_2I_2{\cdot}12AgI)$		
Q = Methane-1,1-bis-methyldiethyl ammonium	0·045	25
= Ethane-1,2-bis-trimethyl ammonium	0·027	25
= Propane-1,3-bis-trimethyl ammonium	0·013	25
= Butane-1,4-bis-trimethyl ammonium	0·027	25
= Pentane-1,5-bis-trimethyl ammonium	0·012	25
= Hexane-1,6-bis-trimethyl ammonium	0·029	25
= Nonane-1,9-bis-trimethyl ammonium	0·014	25
= Decane-1,10-bis-trimethyl ammonium	0·011	25
$QAg_{22}I_{25}$ $(C_nH_mN_3I_3{\cdot}22AgI)$		
Q = Octamethyldiethylenetriammonium	0·058	25
$QAg_5\ I_6(C_nH_mN_4I{\cdot}5AgI)$		
Q = *N*-methylhexamethylenetetramine	0·026	25
$Ag_{2\cdot0}Hg_{0\cdot25}S_{0\cdot5}I_{1\cdot5}$	0·147	25
$Ag_{1\cdot85}Hg_{0\cdot40}Te_{0\cdot65}I_{1\cdot35}$	0·094	25
$Ag_{1\cdot80}Hg_{0\cdot45}Se_{0\cdot70}I_{1\cdot30}$	0·10	25
$Ag_{2\cdot0}Hg_{0\cdot5}Se_{1\cdot0}I_{1\cdot0}$	0·045	25
KAg_4I_4CN	0·14	25
$RbAg_4I_4CN$	0·18	25
$KAg_4I_4CN{\cdot}RbAg_4I_4CN$	0·15	25
$KAg(CN)_2{\cdot}2AgI$	0·029	25
$KAg(CN)_2{\cdot}3AgI$	0·067	25
$KAg(CN)_2{\cdot}4AgI$	0·12	25
$KAg(CN)_2{\cdot}9AgI$	0·038	25
$AgAl_{11}O_{17}$	0·0064	23
Silver ion conductivity of mixed conductors		
$(Ag_2Se)_{0\cdot925}(Ag_3PO_4)_{0\cdot075}$	0·13	25
$(Ag_2S)_{0\cdot69}(Ag_{1\cdot7}Te)_{0\cdot285}(Ag_4P_2O_7)_{0\cdot025}$	0·16	25
$(Ag_2S)_{0\cdot50}(Ag_{1\cdot7}Te)_{0\cdot45}(Ag_3PO_4)_{0\cdot05}$	0·25	25

blocks of oxide ions four layers thick in which the aluminium ions take up both the magnesium and aluminium positions of spinel ($MgAlO_4$), occupying octahedral and tetrahedral interstices. These spinel-like blocks are bound together by loosely packed layers of silver and oxide ions which lie on mirror planes. The silver ions are distributed statistically among the (b) and (d) sites in the mirror planes and an average of 84% of the (d) sites and 43% of the (b) sites are occupied. The silver ion moves two-dimensionally by a collinear interstitialcy mechanism of ion exchange between sites in the widely separated planes. The conductivity of silver beta alumina is shown against the reciprocal of the absolute temperature in Fig. 16.

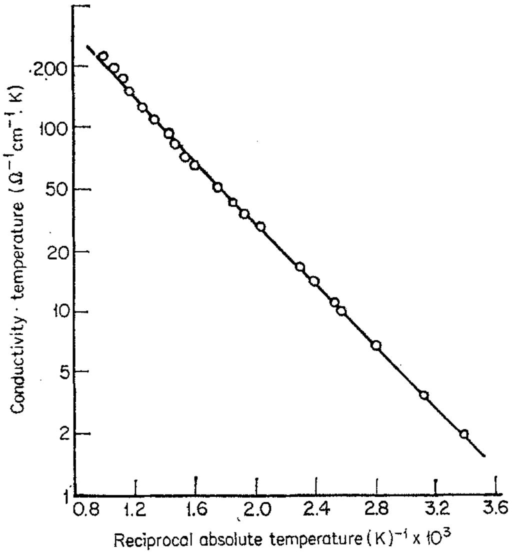

Fig. 16. Conductivity of silver beta alumina.

4. Mixed conductors with silver ion and electron conduction

In this section, the mixed conductor, which has high ionic and electronic conductivities, is described briefly. Silver chalcogenides in the α-phase which are stable at higher temperatures are this sort of mixed conductor [52–59]. Silver chalcogenides in the α-phase have the average structure in which four silver ions are distributed statistically over the available sites of 42 for sulfide and selenide and 36 for telluride. At room temperature, however, they are in the β-phase and have very low ionic conductivity. In order to obtain a high ionic and electronic conductivity solid at room temperature, that is, a solid which has the α-phase silver chalcogenide-like structure at relatively low temperatures, the orthophosphate ion or pyrophosphate ion has been introduced into the lattice of silver chalcogenide.

4.1. *α-silver selenide type conductor*

When silver orthophosphate 5–10 mole % is dissolved in silver selenide, a solid having the α-silver selenide-like structure is obtained at room temperature [60]. For example, when 7·7 mole % of silver orthophosphate is made to react with silver selenide at 800°C, a solid solution is obtained, the ionic conductivity of which is 0·13 $(\Omega\ cm)^{-1}$ at 25°C with the activation energy for ionic conduction of 4·0 kcal $mole^{-1}$. The mixed conductor shows, in general, non-stoichiometry and its total conductivity changes with the cation to anion ratio. Though the change in ionic conductivity with cation to anion ratio is small, it has been recommended to measure the ionic conductivity after the specimen has been equilibrated with pure silver in order to obtain reproducible results. The change of the electronic conductivity with cation to anion ratio in the mixed conductor, however, is relatively large as shown in Fig. 17.

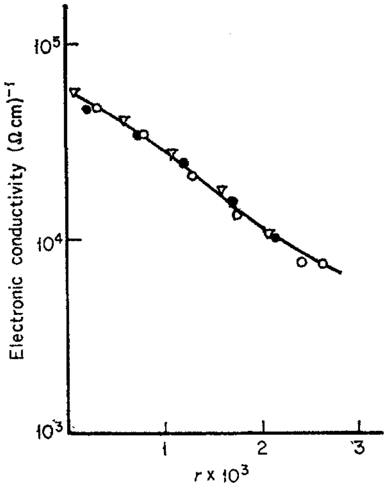

Fig. 17. Electronic conductivity of $(Ag_2Se)_{0.295}(Ag_3PO_4)_{0.075}$. ($r$ = deviation of the cation to anion ratio from that in equilibrium with pure silver.) ● 95°C; ▽ 55°C; ○ 18°C.

4.2. *α-silver sulfide type conductor*

The mixed conductors which have α-silver sulfide like structures at room temperature have been found in the Ag_2S-$Ag_{1\cdot7}Te$-$Ag_4P_2O_7$ and Ag_2S-$Ag_{1\cdot7}Te$-Ag_3PO_4 systems in the composition ranges of Ag_2S 50–80 mole % and $Ag_4P_2O_7$ 2·5–5 mole % for the former system and Ag_2S 50–67 mole % and Ag_3PO_4 5 mole % for the latter system [61]. The highest ionic conductivities are found in the solid solutions of $(Ag_2S)_{0\cdot69}(Ag_{1\cdot7}Te)_{0\cdot285}(Ag_4P_2O_7)_{0\cdot025}$ and $(Ag_2S)_{0\cdot50}(Ag_{1\cdot7}Te)_{0\cdot45}(Ag_3PO_4)_{0\cdot05}$ to be 0·16 $(\Omega\ cm)^{-1}$ and 0·25 $(\Omega\ cm)^{-1}$ at 25°C with activation energies of 3·4 kcal $mole^{-1}$ and 5·1 kcal $mole^{-1}$, respectively. In Fig. 18, the electronic and ionic conductivity of $(Ag_2S)_{0\cdot69}(Ag_{1\cdot7}Te)_{0\cdot29}(Ag_4P_2O_7)_{0\cdot02}$ is shown against the emf of the cell Ag|$RbAg_4I_5$|Sample|Pt which is a measure of the cation to anion ratio in the sample, a large value corresponding to a small ratio of cation to anion.

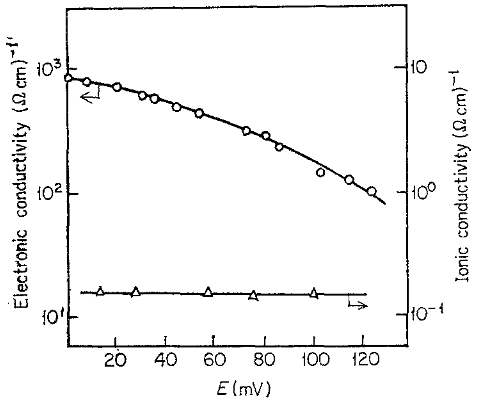

Fig. 18. Ionic and electronic conductivity of $(Ag_2S)_{0\cdot69}(Ag_{1\cdot7}Te)_{0\cdot29}(Ag_4P_2O_7)_{0\cdot02}$ at room temperature. (E = emf of the cell Ag|$RbAg_4I_5$| Sample|Pt.) ○ Electronic conductivity; △ Ionic conductivity.

Summary

The high ionic conductivity solids obtained so far are summarized in Table 1.

It is noteworthy that high ionic conductivity solids have been found at room temperature in very many systems containing the silver ion. Recently, however, copper ion conductors have been found in our laboratory, the copper ion conductivity of which is comparable to that of the high silver ion conductivity solids.

It is to be expected that ionic conductors other than silver ion conductors may be found one after another in the near future at least in the form of monovalent ion conductors.

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