Solid state ionics–The ionic conductivity of the Ag_2S–$Ag_{1.70}Te$–AgX system (AgX; $Ag_4P_2O_7$, Ag_3PO_4 and $AgPO_3$)

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The thermal reaction products in the Ag_2S–$Ag_{1.70}$ Te–$Ag_4P_2O_7$, Ag_2S–$Ag_{1.70}$ Te–Ag_3PO_4 and Ag_2S–$Ag_{1.70}$ Te–$AgPO_3$ systems were found to exhibit both high ionic and electronic conductivity at room temperature. For example, the ionic conductivities of $(Ag_2S)_{0.69}$ $(Ag_{1.70}Te)_{0.285}$ $(Ag_4P_2O_7)_{0.025}$, $(Ag_2S)_{0.5}(Ag_{1.70}Te)_{0.45}$ $(Ag_3PO_4)_{0.05}$ and $(Ag_2S)_{0.65}$ $(Ag_{1.70}$ $Te)_{0.25}$ $(AgPO_3)_{0.1}$ were 0·25, 0·25 and 0·22 (ohm . cm)$^{-1}$ at 25°C, respectively. Differential thermal analysis and X-ray diffraction showed that these high ionic conductivity solids had an α-Ag_2S-like structure at room temperature.

1. Introduction

It is well known that α-Ag_2S which is stable above 176°C is a mixed conductor in which both electrons and ions are mobile [1]. The ionic conductivity of α-Ag_2S is 3×10^0 (ohm . cm)$^{-1}$ at 180°C and the electronic conductivity is 10^2–10^3 (ohm . cm)$^{-1}$ depending on the activity of silver in α-Ag_2S [2]. The high ionic conductivity of α-Ag_2S can be attributed to a peculiar imperfection of the crystal which is typified by an average structure [3]. In α-Ag_2S, the sulphide ions occupy body-centred cubic lattice points, and the silver ions are statistically distributed more or less over the interstitial sites and are able to move from one site to an unoccupied neighbouring one easily. Many other mixed conductors with average structure have been found in the high temperature modifications of silver chalcogenides and copper chalcogenides [4], [1]. The mixed conductor with high ionic conductivity at room temperature, however, has not been reported except the Ag_2Se–Ag_3PO_4 solid solution studied by Takahashi and Yamamoto [5].

The purpose of the present study is to search for high ionic conductivity mixed conductors. A number of systems of silver sulphide and the other silver compounds were studied, and

mixed conductors with high ionic conductivity of $\sigma_i = 2 \times 10^{-1}$ (ohm . cm)$^{-1}$ at room temperature were found in the Ag_2S–$Ag_{1.70}$ Te–AgX; (AgX; $Ag_4P_2O_7$, Ag_3PO_4 and $AgPO_3$) system.

2. Experimental

2.1. *Preparation of starting materials*

Silver sulphide was precipitated by bubbling hydrogen sulphide gas through 1N silver nitrate aqueous solution. The precipitated silver sulphide was washed by distilled water 10 times. Drying treatment was carried out *in vacuo*, and the product was heated at 120°C for 8 h under nitrogen flow.

Silver telluride ($Ag_{1.70}Te$) was prepared from the elements.

Powdered silver (99·999% purity) and powdered tellurium (99·999% purity) which were weighed out in the atomic ratio of 1·70:1·00 were thoroughly mixed before being sealed under vacuum in a Pyrex capsule and the mixture was heated at about 420°C for 24 h.

Silver pyro-, ortho- and metaphosphate were precipitated by mixing the aqueous solution of 1N silver nitrate and the aqueous solutions of
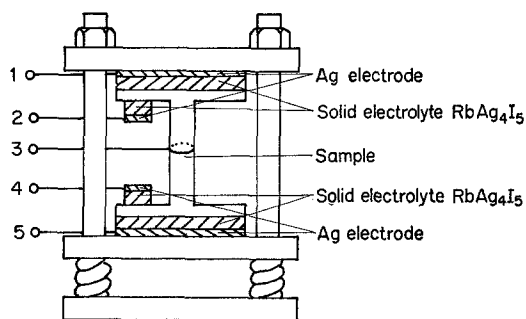
Fig. 1. The cell for ionic conductivity measurements. 1, 2, 4, 5, Ag–lead; 3, Pt–lead.

1N sodium pyrophosphate, disodium hydrogen phosphate and sodium metaphosphate respectively with constant stirring in a dark room. Washing and drying procedures were identical to those used for silver sulphide.

2.2. Synthesis of the specimens for X-ray diffraction and electrical conductivity measurements

A fixed amount of constituent substance was weighed and put in a quartz capsule under vacuum before being heated above its melting temperature (about 810°C) in an electrical furnace. The capsule was cooled slowly to 600°C and then cooled naturally to room temperature. The reaction products were cut out in cylindrical form or pressed to a tablet.

## 2.3. Ionic and electronic conductivity measurements

The ionic conductivity was measured by means of the direct current method [6]. The cell used in this experiment is shown in Fig. 1. The specimen is composed of three parts. The middle cylinder which is about 0·3 cm in diameter and about 1·3 cm long is held between two tablets of about 1·3 cm in diameter and about 0·1 cm thick. In order to eliminate the contact resistance and the polarisation at the interfaces Ag |RbAg₄I₅ and RbAg₄I₅ | specimen, the reference electrodes 2,4 are used. A stabilized direct current is passed through Ag leads 1 and 5 in Fig. 1, and Ag leads 2 and 4 are used for potential difference measurements. In order to change the activity of silver in the sample, the current is passed between silver lead 1 and platinum wire 3 which winds around the sample cylinder.

The electronic conductivity was measured as a function of the silver activity by means of the same method proposed by Miyatani [7]. The planer sample was connected by four platinum probes and two RbAg₄I₅ |Ag electrodes. In order to regulate the silver activity, two RbAg₄I₅ |Ag electrodes and one platinum probe were used. The electronic conductivity was calculated by passing a direct current through two platinum electrodes, measuring the potential fall between two platinum probes.

3. Results

3.1. Ionic conductivity

When a direct current is passed through the cell (I),

$$Ag \mid RbAg_4I_5 \mid sample \mid RbAg_4I_5 \mid Ag \quad (I)$$
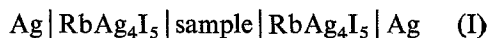
the current is carried practically by the silver ion, because $RbAg_4I_5$ is a pure silver ion conductor [8]. The ionic conductivity σ_i of the sample can be determined by Equation (1),

$$\sigma_i = L \times \frac{I}{E} \quad (1)$$

where L is the length of the sample, E the potential difference and I the current density. A typical E–I plot measured by the arrangement shown in Fig. 1 at room temperature is shown in Fig. 2
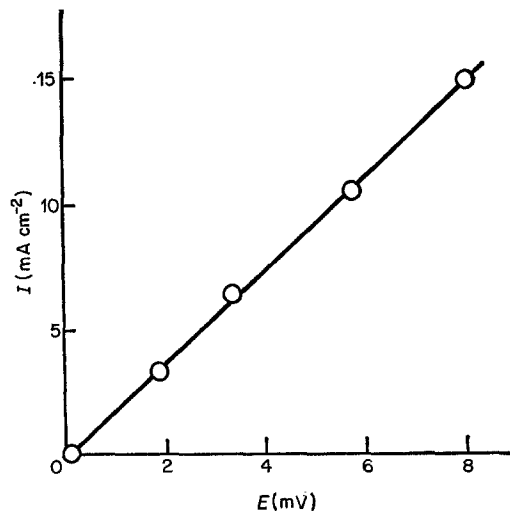

Fig. 2. Voltage (E) versus current density (I) curve of the cell Ag |RbAg₄I₅ | sample P-1 | RbAg₄I₅ | Ag.
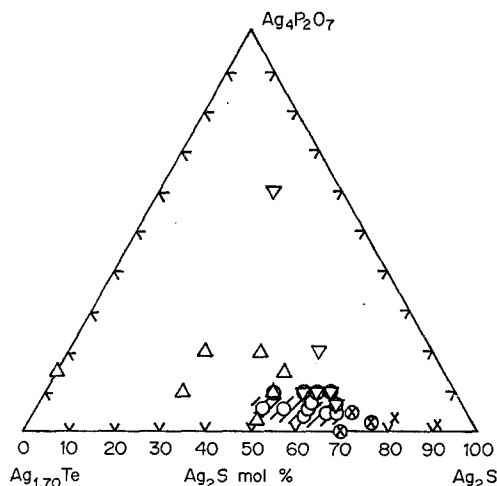
Fig. 3. Results of X-ray study at room temperature of the Ag_2S–$Ag_{1.70}Te$–$Ag_4P_2O_7$ system. $\circ$, α-Ag_2S phase; $\times$, β-Ag_2S phase; $\triangle$, glassy pattern; $\triangledown$, unknown new phase.

Fig. 4. Transition temperature of β-Ag_2S to α-Ag_2S in the Ag_2S–$Ag_{1.70}Te$–$Ag_4P_2O_7$ system.

with regard to the sample of P-1 (Ag_2S 69 mol%, $Ag_{1.70}Te$ 28.5 mol% and $Ag_4P_2O_7$ 2.5 mol%). Fig. 2 represents a good linear relation between I and E, the value of the ionic conductivity being calculated from the slope.

3.2. Ag_2S-$Ag_{1.70}Te$-$Ag_4P_2O_7$ system

3.2. (i) Phase diagram. Fig. 3 shows the phases observed by X-ray diffraction study at room temperature. It was found that a body-centred cubic structure similar to that of α-Ag_2S exists in the composition ranges of Ag_2S 50–69 mol%, $Ag_{1.70}Te$ 29–45 mol% and $Ag_4P_2O_7$ 2.5–5 mol%. The lattice constant of this body-centred cubic structure was 4.94 Å for P-1 (Ag_2S 69 mol%, $Ag_{1.70}Te$ 28.5 mol% and $Ag_4P_2O_7$ 2.5 mol%) at 25°C. The samples in the hatched region in Fig. 3 were found to keep a stable α-Ag_2S-like structure over a year, while the samples containing Ag_2S 70–80 mol%, $Ag_{1.70}Te$ 25–30 mol% and $Ag_4P_2O_7$ 5 mol% had the α-Ag_2S-like structure for only a few days and the structure then transformed to the β-Ag_2S structure (mon.) within a week at room temperature. β-Ag_2S structure was found in the relatively high Ag_2S content ranges of 80–100 mol%. In the lower left part of Fig. 3, the sample was glassy and no X-ray diffraction pattern was observed in the range of $2\theta = 20$–$50°$, while in
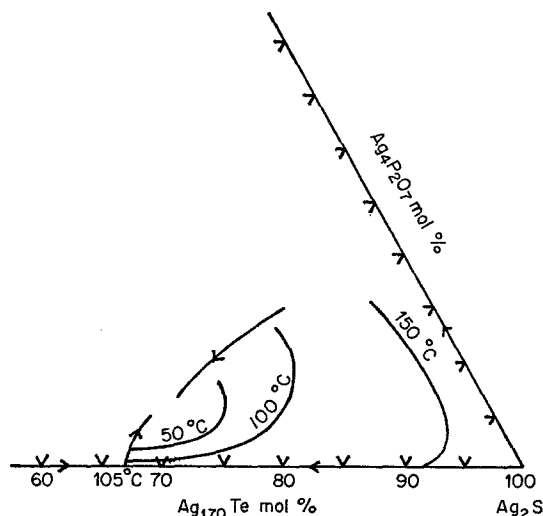
the upper part of Fig. 3, there was a new phase, the X-ray diffraction patterns of which were broad and complex. In order to confirm the phase region in which the α-Ag_2S-like structure exists stably in the Ag_2S–$Ag_{1.70}Te$–$Ag_4P_2O_7$ system, the transition temperature of the β-Ag_2S phase was measured by the change of resistance and differential thermal analysis, DTA, in the Ag_2S–rich composition region as a function of the composition. Fig. 4 shows the transition temperature of β-Ag_2S to α-Ag_2S phase. As shown in Fig. 4, the transition temperature decreased with increasing $Ag_{1.70}Te$ and $Ag_4P_2O_7$ contents. The binary eutectoid point in the Ag_2S-$Ag_{1.70}Te$ system was about 105°C at 67 mol% Ag_2S, while in the Ag_2S–$Ag_4P_2O_7$ system it was not determined, because the β–α transition peak in the DTA pattern became smaller with increasing $Ag_4P_2O_7$ content and disappeared above
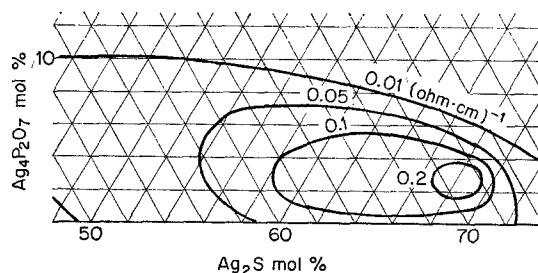

Fig. 5. Ionic conductivity of the Ag_2S–$Ag_{1.70}Te$–$Ag_4P_2O_7$ system at room temperature.
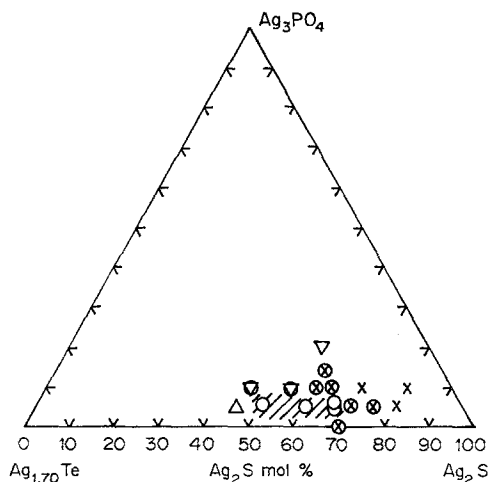
Fig. 6. Results of X-ray study at room temperature of the $Ag_2S-Ag_{1.70}Te-Ag_3PO_4$ system. ○, α-Ag_2S; ×, β-Ag_2S; △, glassy pattern; ▽, unknown new phase.

30 mol% $Ag_4P_2O_7$. In the $Ag_2S-Ag_{1.70}Te-$ $Ag_4P_2O_7$ ternary system, the transition temperature decreased rapidly along the eutectoid line; the ternary eutectoid point was below room temperature at about Ag_2S 68 mol%, $Ag_{1.70}Te$ 27 mol% and $Ag_4P_2O_7$ 5 mol%. It may be concluded from these experimental results, that the phase with α-Ag_2S–like structure is not a new compound but the solid solution of Ag_2S with $Ag_{1.70}Te$ and $Ag_4P_2O_7$. The melting temperature of the sample P-1 was about 710°C.

3.2. (ii) Ionic conductivity. The ionic conductivities of the samples with the α -Ag_2S-like structure were measured as a function of the composition. Fig. 5 shows the isothermal conductivity profiles at 25°C. The samples contain-
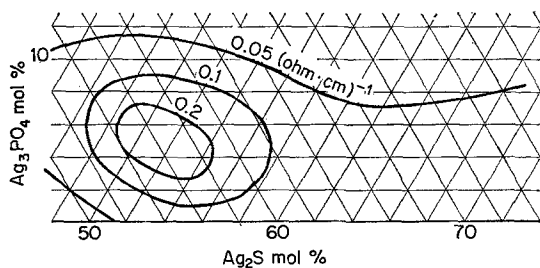

Fig. 7. Ionic conductivity at room temperature of the $Ag_2S-Ag_{1.70}Te-Ag_3PO_4$ system.

ing Ag_2S 58–70 mol%, $Ag_{1.70}Te$ 27–39 mol% and $Ag_4P_2O_7$ 1–5 mol% have high ionic conductivities of greater than 10^{-1} (ohm . cm)$^{-1}$. The highest value was found to be 0·25 (ohm . cm)$^{-1}$ at the composition near Ag_2S 69 mol%, $Ag_{1.70}Te$ 28·5 mol% and $Ag_4P_2O_7$ 2·5 mol% (sample P-1).

3.3. $Ag_2S-Ag_{1.70}Te-Ag_3PO_4$ system

Figure 6 shows the phases observed by X-ray diffraction studies of the $Ag_2S-Ag_{1.70}Te-$ Ag_3PO_4 system at room temperature. As shown in Fig. 6, the α-Ag_2S-like phase appears in the composition range of Ag_2S 50–67 mol%, $Ag_{1.70}Te$ 28–45 mol% and Ag_3PO_4 5 mol%. The lattice constant of the α-Ag_2S-like phase was 4·92 Å at 25°C for the sample O–11 (Ag_2S 50 mol%, $Ag_{1.70}Te$ 45 mol% and Ag_3PO_4 5 mol%). The X-ray diffraction patterns of the samples in the lower left part of Fig. 6 showed broad lines, and, in the right part, the lines of β-Ag_2S (mon.). The samples in the upper part gave new phase X-ray diffraction patterns, which were different from those of the corresponding new phase observed in the $Ag_2S-Ag_{1.70}Te-$ $Ag_4P_2O_7$ system. The crystal structure of this new phase could not be determined because the patterns were broad.

The results of ionic conductivity measurements of the samples having an α-Ag_2S-like phase at room temperature are shown in Fig. 7. As can be seen in Fig. 7, the samples containing Ag_2S 47–58 mol%, $Ag_{1.70}Te$ 38–48 mol% and Ag_3PO_4 1–9 mol% had ionic conductivities of greater than 10^{-1} (ohm . cm)$^{-1}$. The sample O–11 (Ag_2S 50 mol%, $Ag_{1.70}Te$ 45 mol% and Ag_3PO_4 5 mol%) had the highest ionic conductivity of $2·5 \times 10^{-1}$ (ohm . cm)$^{-1}$. The phase having the α-Ag_2S-like structure and high ionic conductivity might be the solid solution of α-Ag_2S with $Ag_{1.70}Te$ and Ag_3PO_4, similar to the situation in the $Ag_2S-Ag_{1.70}Te-Ag_4P_2O_7$ system.

3.4. $Ag_2S-Ag_{1.70}Te-AgPO_3$ system

Fig. 8 shows the phases observed by X-ray diffraction studies of the $Ag_2S-Ag_{1.70}Te-$ $AgPO_3$ system at room temperature. The phase

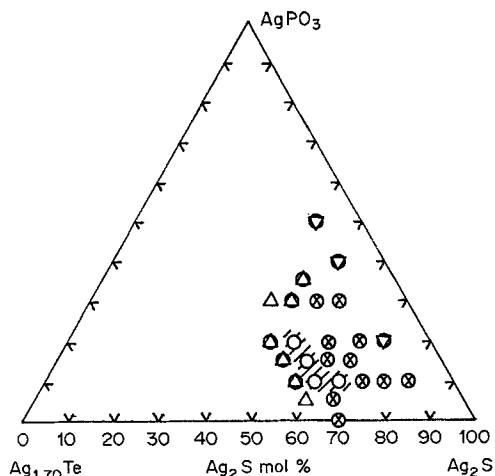Fig. 8. Results of X-ray study at room temperature of the $Ag_2S–Ag_{1.70}Te–AgPO_3$ system. ○, α-Ag_2S; ×, β-Ag_2S; △, glassy pattern; ▽, unknown new phase.

having the α-Ag_2S-like structure existed in relatively high $AgPO_3$ content regions. The lattice constant of the sample M-10 (Ag_2S 60 mol%, $Ag_{1.70}Te$ 30 mol% and $AgPO_3$ 10 mol%) was 4·96 Å at 25°C.

The X-ray diffraction patterns of the sample in the left part of Fig. 8 showed that the samples were glassy, while those of lower right part showed β-Ag_2S (mon.).
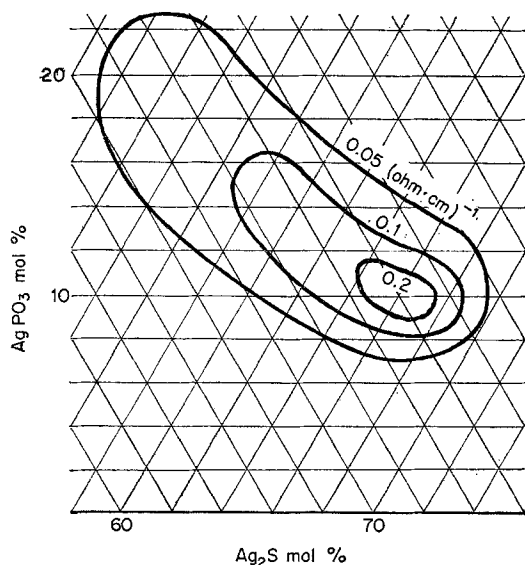
The isothermal ionic conductivity in this

Fig. 9. Ionic conductivity at room temperature of the $Ag_2S–Ag_{1.70}Te–AgPO_3$ system.
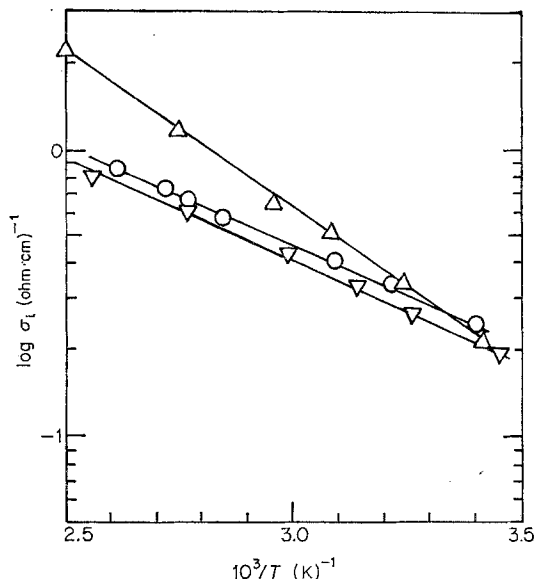

Fig. 10. Temperature dependence of ionic conductivity. ○, P-1; △, O-11; ▽, M-23.

system is shown in Fig. 9 at 25°C. The composition showing the highest ionic conductivity of $2·2 \times 10^{-1}$ (ohm . cm)$^{-1}$ was M-23 (Ag_2S 65 mol%, $Ag_{1.70}Te$ 25 mol% and $AgPO_3$ 10 mol%.).

3.5. Temperature dependence of ionic conductivity

The temperature dependence of ionic conductivity was determined for the samples with high ionic conductivity in the above three systems. The results for P-1, O-11 and M-23 are shown in Fig. 10. The ionic conductivities of the samples investigated in this study were comparable to that of $RbAg_4I_5$. The highest value of ionic conductivity was found in O–11 in the Ag_2S–$Ag_{1.70}Te$–Ag_3PO_4 system to be $2·2 \times 10^{-1}$ (ohm . cm)$^{-1}$ at 20°C and $2·2 \times 10^{0}$ (ohm . cm)$^{-1}$ at 127°C. The ionic conductivity increased linearly with decreasing reciprocal of absolute temperature. The activation energies for ionic conduction were calculated from the slopes of the linear plots of log. σ_i versus $1/T$ to be 0·13 eV for P-1, 0·22 eV for O-11 and 0·14 eV for M-23 respectively. These values of activation energy were similar in magnitude to those of high ionic conductivity solid electrolytes which are 0·17 eV for Ag_3SI [9] and 0·07 eV for $RbAg_4I_5$ [8]. The mechanism of cation transport in the samples

Table 1. Results of X-ray study at room temperature of the $Ag_2S-Ag_xTe-Ag_4P_2O_7$ system.

Sample number	x	Composition in mole ratio			Phase determined by X-ray study
		Ag_2S	Ag_xTe	$Ag_4P_2O_7$	
2	2·0	69	28·5	2·5	α-Ag_2S + β-Ag_2S(glassy)
4	2·0	63	27	10	Glassy
5	1·9	69	28·5	2·5	α-Ag_2S(glassy)
P-1	1·7	69	28·5	2·5	α-Ag_2S
6	1·5	69	28·5	2·5	α-Ag_2S + β-Ag_2S

having an α-Ag_2S-like structure, therefore, would be similar to that in these other high ionic conductivity solid electrolytes.

4. Discussion

Miyatani [10] reported that in the Ag_2Te-Ag_2S system the α-Ag_2S phase is stable at room temperature, while Takahashi et al. [11] investigated recently the ionic conductivity of the Ag_2S-Ag_2Te system, and reported that the α-Ag_2S solid solution is stable only above 60°C in the composition of about 80 mol% Ag_2S and 20 mol% Ag_2Te. When silver pyrophosphate was added to this eutectoid composition, the α-Ag_2S-like X-ray diffraction patterns were not obtained but the patterns of glassy β-Ag_2S were recognized. When $Ag_{1.70}Te$ was used in place of Ag_2Te, however, the α-Ag_2S phase was found to exist at room temperature. The phases observed by X-ray diffraction analysis of the $Ag_2S-Ag_xTe-Ag_4P_2O_7$ ($x = 1·50-2·00$) system are

shown in Table 1. In the $Ag-Ag_2Te$ system, the existence of the second intermediate phase $Ag_{5-\delta}Te_3$ was reported, where δ was negligibly small [12]. The composition of $Ag_{5-\delta}Te_3$ coincides almost with that of $Ag_{1.70}Te$. Therefore, the α-Ag_2S phase should be stable at room temperature in the $Ag_2S-Ag_{5-\delta}Te-Ag_4P_2O_7$ system, as can be seen in Fig. 4.

The electrical conductivities of some mixed conductors and high ionic conductivity solid electrolytes are summarized in Table 2. It should be noted from Table 2 that the ionic conductivities of the α-Ag_2S phase were very high and comparable to that of high ionic conductivity solid electrolytes at room temperature. The remarkable feature of the α-Ag_2S phase is the fact that the electronic conductivity is dependent on the activity of silver in the sample, while the ionic conductivity is not. The electronic and ionic conductivities of P-1 at 20°C are shown in Fig. 11 as a function of the activity of silver in the sample. The activity of silver, a, in the sample is

Table 2. The electrical conductivities of some mixed conductors and ionic conductors.

Substance	Temperature (°C)	Ionic conductivity (ohm . cm)$^{-1}$	Activation energy (eV)	Electronic conductivity (ohm . cm)$^{-1}$	Reference
α-Ag_2S	180	3×10^0		$10^3 - 10^2$	2
α-Ag_2Te	160	7×10^{-1}		$(6-1) \times 10^2$	2
α-Ag_2S(s.s.)*					
P-1	25	$2·5 \times 10^{-1}$	0·13	$(8·5-1·8) \times 10^2$	
O-11	25	$2·5 \times 10^{-1}$	0·22		
M-23	25	$2·2 \times 10^{-1}$	0·14		
α-Ag_2Se(s.s.)*	25	$1·3 \times 10^{-1}$	0·17	$(1·8-0·8) \times 10^3$	5
$RbAg_4I_5$**	25	$2·4 \times 10^{-1}$	0·07		8
Ag_3SI**	25	1×10^{-2}	0·17		9

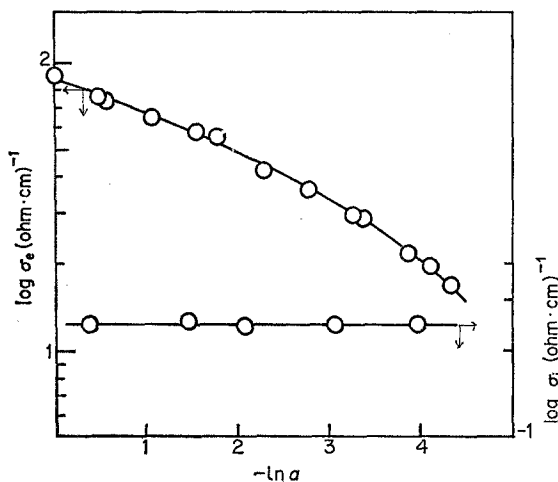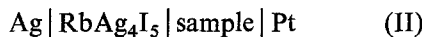* Solid solution
** Ionic conductor

Fig. 11. Electronic conductivity σ_e and ionic conductivity σ_i versus activity of silver of the sample P-1 at 20°C.

determined as follows by the use of cell (II).

$$-RT \ln a = EF \qquad (2)$$

$$Ag \,|\, RbAg_4I_5 \,|\, sample \,|\, Pt \qquad (II)$$

where E is the emf of the cell (II). As shown in Fig. 11, the electronic conductivity was changed from 8.5×10^2 (ohm . cm)$^{-1}$ to 1.8×10^2 (ohm . cm)$^{-1}$ by the activity of silver in the sample, while the ionic conductivity was constant at 2.4×10^{-1} (ohm . cm)$^{-1}$.

5. Conclusion

The results obtained from the studies on the Ag_2S–$Ag_{1.70}Te$–AgX (AgX; $Ag_4P_2O_7$, Ag_3PO_4 and $AgPO_3$) system led to the following conclusions:

(1) The α-Ag_2S phase could be stabilized at room temperature by the formation of the solid solution of Ag_2S with $Ag_{1.70}Te$ and $Ag_4P_2O_7$, Ag_3PO_4 or $AgPO_3$. The composition regions of the solid solutions were Ag_2S 70–80 mol%,

$Ag_{1.70}Te$ 25–30 mol% and $Ag_4P_2O_7$ 5 mol% in the Ag_2S–$Ag_{1.70}Te$–$Ag_4P_2O_7$ system, Ag_2S 50–67 mol%, $Ag_{1.70}Te$ 28–45 mol% and Ag_3PO_4 5 mol% in the Ag_2S–$Ag_{1.70}Te$–Ag_3PO_4 system, and Ag_2S 50–65 mol%, $Ag_{1.70}Te$ 25–35 mol% and $AgPO_3$ 10–20 mol% in the Ag_2S–$Ag_{1.70}Te$–$AgPO_3$ system.

(2) Ionic conductivity higher than 10^{-1} (ohm . cm)$^{-1}$ was obtained in the α-Ag_2S phase stable region. The compositions exhibiting the highest ionic conductivity were P-1 (Ag_2S 69 mol%, $Ag_{1.70}Te$ 28·5 mol% and $Ag_4P_2O_7$ 2·5 mol%), O-11 (Ag_2S 50 mol%, $Ag_{1.70}Te$ 45 mol% and Ag_3PO_4 5 mol%) and M-23 (Ag_2S 65 mol%, $Ag_{1.70}Te$ 25 mol% and $AgPO_3$ 10 mol%). The highest value of 2.5×10^{-1} (ohm . cm)$^{-1}$ was obtained for O-11 and P-1 at room temperature.

(3) The ionic conductivities increased linearly on decreasing the reciprocal of the absolute temperature. The value of the activation energy for ionic conduction was about 0·2 eV, which is comparable to that of other silver-containing high ionic conductivity solid electrolytes.

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