Electrical Conductivities of Silver Copper Sulfide, $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$

Shoichiro IKEDA,* Norio MATSUDA*, Genkichi NAKAGAWA*
and Kaname ITO*

Silver copper sulfide, Jalspaite $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$, is a functional material occurring in the mixed sulfide of silver and copper prepared as an active material for a copper (II) ion-selective electrode. In the present paper, electrical conductivities and transport numbers of the pure silver copper sulfide synthesized from the elements are measured with a conventional AC bridge method, Wagner's method and Tubandt's electrolytic method, respectively. It is clarified that silver copper sulfide is the mixed conductor of which total electrical conductivities are 1.6×10^{-4} and $3.5 \times 10^{-3} \text{ S cm}^{-1}$ at 25 and 100°C and transport numbers of silver ions, copper (I) ions, and electrons are 0.69, 0.30, and 0.01, at 25°C and 0.77, 0.19, and 0.04, at 100°C, respectively.

1 Introduction

In previous works^{1,2)}, the structural properties of the mixed sulfide of silver and copper as an active material for a copper (II) ion-selective electrode were investigated by X-ray diffraction analysis, and then it was found that silver copper sulfide, $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$, would be present in the active materials prepared by the simultaneous precipitation method and that this compound would play an important role in the response of the electrode.

This compound, $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$, is one of naturally occurred minerals of the ternary system Ag-Cu-S and is called Jalspaite. The phase diagram of the ternary system and the lattice parameters of the some sulfides involving Jalspaite have been investigated using microscopic and X-ray techniques by Schwartz³⁾, Suhr⁴⁾, and Djurle⁵⁾ in detail. The electrical resistivity change with the phase transformation of the system $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}$ has been studied by Graf⁶⁾, but the detailed electrical properties of this compound have never been reported.

In the present paper, electrical conductivities and transport numbers of silver copper sulfide synthesized from the elements are measured

and electrical properties of this compound will be clarified.

2 Experimental

2.1 Preparation of materials

Silver copper sulfide, $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$, was directly synthesized from the elements such as silver, copper, and sulfur, that is, the powders of these elements were mixed and well ground in an agate mortar with the molar ratio of 1.55 : 0.45 : 1.00 and the mixture was sealed in an evacuated Pyrex tube and then heated at 400°C for about 5 h in an electric furnace. The formation of the compound was verified by powder X-ray diffraction analysis. KAg_4I_9 , RbAg_4I_9 , and $7\text{CuBr} \cdot \text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$ were prepared according to the procedures of original papers^{7,8)}. All chemicals used were of reagent grade without further purification.

2.2 Conductivity measurements and Wagner's method

Samples for the electrical conductivity measurements were prepared by molding this compound finely powdered into a disk with 11 mm diameter and about 3 mm thickness at a pressure of 0.245 MPa. Electrodes for total electrical conductivity measurements were made of graphite powder which were simultaneously compressed to both sides of the disk-shaped sample in order to reduce the contact resistance. Platinum sheets were used as current collectors.

* Department of Synthetic Chemistry, Nagoya Institute of Technology (Gokiso-cho, Showa-ku, Nagoya)

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Total conductivities were measured by the conventional method using a 1 kHz impedance bridge, YEWE, model BV-Z-13A.

For silver ionic conductivity measurements, the following cell was constructed, Ag/Ag powder+RbAg₄I₅/RbAg₄I₅/Ag_{1.55}Cu_{0.45}S/RbAg₄I₅/Ag powder+RbAg₄I₅/Ag. Two disks of RbAg₄I₅ which were simultaneously compressed to both sides of the sample instead of the graphite electrodes were used as the barrier of electronic conduction according to the direction of Wagner⁹⁾. A stabilized direct current was passed through the cell and the silver ionic conductivities were calculated from the *IR* drops on the cell, since the silver ionic conductivity of RbAg₄I₅ is about 1000 times as large as the sample and the resistance of RbAg₄I₅ layers is negligible.

The electronic conductivities of silver copper sulfide were measured by Wagner's polarization method⁹⁾. The cathode of the polarization cell was a mixture of silver and copper powders with the molar ratio of 1.55 : 0.45; (31 : 9), and the anode was a graphite disk. A small stabilized direct current was applied to the cell and the cell voltages were measured at various current densities.

2.3 Tubandt's electrolytic method

Transport numbers of charge carriers in Jalspaite were also measured by Tubandt's electrolytic method¹⁰⁾. The cell for this measurement was constructed of a platinum cathode, a disk of KAg₄I₅, three disks of Ag_{1.55}Cu_{0.45}S and a silver anode as shown in Fig. 1. In the cell, KAg₄I₅ was used as a solid electrolyte with pure silver ionic conduction.

A constant direct current was passed through

Fig. 1 Schematic diagram of a circuit for transport number measurements by Tubandt's method

this cell in nitrogen atmosphere. The current adopted was either 70 or 400 μAcm^{-2} according to the temperature. Then the weight deviation of each layer in the cell was measured and a quantity of electricity was measured by using an electronic coulometer, Hokuto Denko, model HF-102.

3 Results and Discussion

According to the X-ray diffraction studies reported by Djurle,⁵⁾ silver copper sulfide, Jalspaite Ag_{1.55}Cu_{0.45}S, has a body-centered tetragonal lattice at room temperature and transforms into a body-centered cubic lattice at 112°C and also into a face-centered cubic lattice at about 300°C¹¹⁾. Its resistance suddenly decreases at a transformation temperature of 117 to 120°C⁵⁾. In the present paper, the electrical conductivities and transport numbers were measured in the range of 20 to 103°C where a single phase of tetragonal lattice would be occurred in this compound.

The total electrical conductivities, σ_t , of silver

Fig. 2 Electrical conductivities of silver copper sulfide, Ag_{1.55}Cu_{0.45}S
○ : Total, □ : Silver ionic, --- : Copper (I) ionic, △ : Electronic (hole)

Fig. 3 Polarization curves of the cell, Ag + Cu (1.55: 0.45) | Ag_{1.55}Cu_{0.45}S | Graphite, for electronic (hole) conductivity measurements by Wagner's method

copper sulfide obtained are shown in Fig. 2 where $\log \sigma_t$ is plotted as a function of the reciprocal absolute temperature. They were 1.6×10^{-4} and 3.5×10^{-2} S cm⁻¹ at 25 and 100°C, respectively, and were the same order of magnitude as that of silver sulfide, β -Ag₂S⁽¹¹⁾.

Silver ionic conductivities of silver copper sulfide are also shown in Fig. 2. They were 1.1×10^{-4} and 2.7×10^{-3} S cm⁻¹ at 25 and 100°C, respectively and were about 69 to 77% of total conductivities in the temperature range observed.

Figure 3 shows the polarization curves of the cell for electronic conductivity measurements at various temperatures by Wagner's method. These curves were not straight lines so that Wagner's equation could not be utilized to calculate electronic conductivities. Therefore, Takahashi-Yamamoto's modified equation (1)⁽²⁾ was used,

$$I = \sigma_+ \{ \exp(kEF/RT) - 1 \} RT/kLF \quad (1)$$

where k is a correction factor determined by trial and error, I a current density, σ_+ an electronic (hole) conductivity, L thickness of the sample, E a cell voltage, and the others conventional signs.

Fig. 4 Relationships between $\log I$ and $\log \{ \exp(kEF/RT) - 1 \}$ for calculation of electronic (hole) conductivities

Figure 4 shows the relationships between $\log I$ and $\log \{ \exp(kEF/RT) - 1 \}$ and also k 's values. The electronic conductivities calculated from these curves are also shown in Fig. 2. They were 2.5×10^{-6} and 1.5×10^{-4} S cm⁻¹ at 25 and 100°C, respectively, and were about 2 to 4% of total conductivities.

Copper ionic conductivities of silver copper sulfide could not be measured directly, because the pure copper (I) ionic conductor, $7\text{CuBr} \cdot \text{C}_6\text{H}_{12}\text{N}_4\text{CH}_2\text{Br}$, used as the barrier for silver ions and electrons could not stop the diffusion of silver ions due to the substitution of Ag ions for Cu ions. Therefore, the copper ionic conductivities were estimated by subtracting silver

Table 1 Transport numbers in silver copper sulfide, Ag_{1.55}Cu_{0.45}S, calculated from the data of conductivity measurements

Charge carrier	Temperature	
	25°C	100°C
Ag ⁺ ion	0.69	0.77
Cu ⁺ ion	0.30	0.19
electron (hole)	0.01 ₆	0.04 ₂

Table 2 Transport numbers in silver copper sulfide, $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$, obtained by Tubandt's electrolytic method

(a) Experimental data		
Operating temp.	37°C	98°C
Current density	70 μAcm^{-2}	400 μAcm^{-2}
Quantity of electricity, Q	51.5000 C	80.0000 C
Ag-equivalent	57.57 mg	89.424 mg
Cell construction	Change of mass (mg)	
$\oplus\text{Ag}$ -anode $\left. \begin{array}{l} \text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}_{-\text{I}} \\ \text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}_{-\text{II}} \\ \text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}_{-\text{III}} \\ \text{KAg}_4\text{I}_5 \\ \ominus\text{Pt-cathode} \end{array} \right\}$	$\left. \begin{array}{l} -56.69 \pm 0.01 \\ 0.00 \pm 0.01 \\ +56.26 \pm 0.01 \end{array} \right\}$ $(\Delta \bar{W}_{\text{I}})$	$\left. \begin{array}{l} -86.18 \pm 0.01 \\ 0.00 \pm 0.01 \\ +85.89 \end{array} \right\}$ $(\Delta \bar{W}_{\text{I}})$
Whole cell (ΔW_e)	-0.43 ± 0.01	-0.29 ± 0.01
(b) Transport numbers calculated		
Carrier	Transport numbers	
Ag^+ ion	0.972	0.948
Cu^+ ion	0.022	0.049
Electron	0.006	0.003

ionic and electronic conductivities from the total electrical conductivities, and they are shown in Fig. 2 by the broken line. They were 4.8×10^{-5} and $6.5 \times 10^{-4} \text{ S cm}^{-1}$ at 25 and 100°C, respectively, and about 30 to 19% of the total conductivities.

The transport numbers of charge carriers in silver copper sulfide estimated from the data of conductivities, as shown in Fig. 2, were summarized in Table 1.

The data of the transport numbers obtained by Tubandt's method are also shown in Table 2-(a). The calculating procedure of this method was carried out as follows, according to Tubandt¹⁹⁾.

At first, a transport number of electrons, t_e , in this compound was calculated from a weight loss of a whole cell, ΔW_e , according to the following equation (2);

$$t_e = \Delta W_e F / Q M_I \quad (2)$$

where M_I is atomic weight of iodine and Q a quantity of electricity passed through the cell.

It was considered that a weight loss of a whole cell would be caused by sublimation of iodine deposited by electrolysis at the interface between the KAg_4I_5 layer and the $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ -III layer which was in turn operating as an anode. And ΔW_e will correspond to a quantity of electricity due to the electronic conduction in silver copper sulfide.

On the other hand, the weight loss, ΔW_I , of the $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ -I layer and the Ag anode may be considered to be caused by ionic conduction in silver copper sulfide, but ΔW_I observed could not be accounted with the conduction of only Ag^+ ions, because ΔW_I was not equal to the Ag-equivalent for coulombs passed.

Therefore, the ionic current in Japelite was considered to be carried by not only Ag^+ ions but also Cu^+ ions, so that ΔW_I could be represented by the equation as follows,

$$\Delta W_I = (t_{\text{Ag}^+} M_{\text{Ag}} + t_{\text{Cu}^+} M_{\text{Cu}}) Q / F \quad (3)$$

where t_{Ag^+} and t_{Cu^+} are transport numbers of Ag^+ ion and Cu^+ ion, and M_{Ag} and M_{Cu} atomic weights of silver and copper, respectively. Following relationship should also be fulfilled according to the definition of transport numbers because sulfur ions do not move in such a solid electrolyte,

$$t_{\text{Ag}^+} + t_{\text{Cu}^+} + t_e = 1 \quad (4)$$

From the equations (3) and (4), t_{Ag^+} and t_{Cu^+} will be derived as follows,

$$t_{\text{Ag}^+} = \{ (\Delta W_I F / Q) - M_{\text{Cu}} (1 - t_e) \} / (M_{\text{Ag}} - M_{\text{Cu}}) \quad (5)$$

$$t_{\text{Cu}^+} = \{ (\Delta W_I F / Q) - M_{\text{Ag}} (1 - t_e) \} / (M_{\text{Cu}} - M_{\text{Ag}}) \quad (6)$$

The transport numbers of Ag^+ ion, Cu^+ ion and electron calculated from the experimental data by the equations (2), (5), and (6) were 0.972, 0.022, and 0.006 at 37°C and 0.948, 0.049, and 0.003 at 98°C, respectively, as shown in Table 2-(b).

These values were different from those obtained by conductivity measurements. The reason was considered to be as follows. The motion of copper (I) ions was suppressed by the KAg_4I_5 layer as a solid electrolyte because copper ions could not be substituted for Ag ions in KAg_4I_5 and the motion of electrons was also suppressed by the reaction polarization of deposition of iodine by the electrolysis of KAg_4I_5 , so that apparent transport numbers of copper (I)

ions and electrons obtained by Tubandt's method became to smaller values than those obtained by conductivity measurements.

Accordingly, it would be concluded that the values of transport numbers in silver copper sulfide estimated from the results of the conductivity measurements were reasonable, and were 0.69, 0.30, and 0.01₆ at 25°C and 0.77, 0.19, and 0.04₂ at 100°C for silver ions, copper ions, and electrons, respectively. And also the ratio of transport numbers between silver and copper (I) ions was comparable to the molar fraction in Jالpaite, namely 0.775:0.225.

Such electrical properties of this compound, especially the fact that ionic carriers are not only Ag⁺ ions but also Cu⁺ ions, are applicable to account the response mechanism of a copper (II) ion-selective electrode with a solid state membrane of the silver and copper mixed sulfide involving this compound. The mechanism, however, will be reported at next opportunity.

4 Summary

Silver copper sulfide, Jالpaite Ag_{1.55}Cu_{0.45}S, occurring in the mixed sulfide of silver and copper as an active material for a copper (II) ion-selective electrode, was synthesized by the direct reaction between the elements and the electrical conductivities and transport numbers of this compound were measured. The following results were obtained.

The total electrical conductivities of silver copper sulfide were 1.6×10^{-4} and 3.5×10^{-3} S cm⁻¹ at 25 and 100°C, respectively, and

transport numbers of silver ion, copper (I) ion and electron in this compound were 0.69, 0.30, and 0.01₆ at 25°C and 0.77, 0.19, and 0.04₂ at 100°C, respectively, according to Wagner's method.

Accordingly, it may be concluded that silver copper sulfide will be the mixed conductor with silver and copper (I) ionic conductions having the same order of transport numbers as the molar ratio and a slight electronic conduction.

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