

Ionic Conductivity and Coulometric Titration of Copper Selenide

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The ionic conductivity of copper selenide was measured in the temperature range of 30–180°C by blocking the electronic current by the copper ion high conductivity solid electrolyte, $37\text{CuBr}\cdot 3[\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{CH}_3\text{Br}]$. It was found that the α -phase of $\text{Cu}_{2-\delta}\text{Se}$ has a high ionic conductivity; for example, $\text{Cu}_{1.75}\text{Se}$ exhibited an ionic conductivity of $3 \times 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$ at room temperature. The coulometric titration of copper selenide was carried out with the help of the cell, $\text{Au}/\text{Cu}_{2-\delta}\text{Se}/\text{solid electrolyte}/\text{Cu}$; from the temperature dependence of the cell voltage, the β - α transition temperatures of $\text{Cu}_{2-\delta}\text{Se}$ were determined as a function of δ .

1. Introduction

Materials exhibiting high ionic and electronic conductivity are interesting in view of the physical meanings and their applications to electrical devices. Copper (*I*) selenide has been known to have nonstoichiometric composition, $\text{Cu}_{2-\delta}\text{Se}$, and to exhibit mixed conductivity (partly ionic and partly electronic) similar to silver chalcogenides (*1-6*).

Copper selenide has two modifications (α and β phase). The α -phase (high temperature phase with cubic lattice) has the so-called average structure, in which cations are distributed statistically on the interstitial sites, and it is expected to have high ionic conductivity. However, the ionic conductivity of copper chalcogenides has not been reported except at high temperature (*7, 8*). The stoichiometric compound, Cu_2Se , transforms from β -phase (low temperature phase) to α -phase near 110°C. The transition temperature decreases with increasing deviation, δ , from the stoichiometric composition and in the range of $\delta > 0.15$, α -phase exists at room temperature. The phase diagram of this Cu–Se system has been reported by several authors, but their diagrams do not coincide with each other (*9-11*).

In our laboratory, the ionic conductivity of copper selenide was measured by using the copper ion solid electrolyte, $37\text{CuBr}\cdot 3[\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{CH}_3\text{Br}]$, which had been discovered in our laboratory (*12*), and the relation between the ionic conductivity and the deviation from stoichiometric composition was investigated. The coulometric titration of copper selenide was carried out by the method proposed by Wagner (*13*) using copper ion solid electrolyte. The phase diagram of the Cu–Se system is discussed.

2. Experimental

2.1. Preparation of Copper Selenide and Solid Electrolyte, $37\text{CuBr}\cdot 3[\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{CH}_3\text{Br}]$

Copper selenide was prepared from elements. Powdered copper and selenium (99.999%) were mixed thoroughly in the atomic ratio of 2- δ :1 before being sealed under vacuum in a Pyrex capsule. The mixture was heated at about 200°C for 48 hr and, after pressing into a pellet, it was heated again at about 400°C for 48 hr.

The solid electrolyte, $37\text{CuBr}\cdot 3[\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{CH}_3\text{Br}]$, was prepared according to the method described previously (*12*). The mixture of copper(*I*) bromide and *N,N'*-dimethyl-

triethylenediamine dibromide (92.5:7.5 mole ratio) was thoroughly ground and then heated in a sealed evacuated Pyrex vessel at 200°C for 17 hr.

2.2. Ionic Conductivity Measurement

The ionic conductivity was measured with the help of the cell shown in Fig. 1, which is similar to that used for silver chalcogenides and blocks the electronic contribution by the copper ion conductor (5). The cell is composed of three tablets. The middle tablet, which is a part of the sample about 1.0 cm in diameter and about 1.0 cm thick, is held between two tablets, which are about 1.3 cm in diameter and about 0.2 cm thick. The latter tablets both have the arrangements of Cu⁺ electrolyte/electrolyte/sample. To eliminate the contact resistance and the polarization at the interfaces of Cu/electrolyte and electrolyte/sample, reference electrodes 2 and 4 are used. A stabilized direct current is passed through Ag plates 1 and 5, and the potential difference between the reference electrodes 2 and 4 was measured. In order to change the atomic ratio of copper to selenium in the sample, a current is passed between silver plates 1 and 5 and platinum wire 3 which is wound around the sample cylinder.

2.3. Coulometric Titration

The activity of copper in the sample was determined as a function of the cation-anion ratio by means of coulometric titration, the principle of which was reported by Wagner (13), using the cell, Cu/solid electrolyte/sample

/Au. In this study, the copper-ion high-conductivity solid electrolyte, $37\text{CuBr} \cdot 3[\text{C}_6\text{H}_{12}\text{N}_2 \cdot 2\text{CH}_3\text{Br}]$, was used to carry out the coulometric titration of copper selenide in the temperature range 25–200°C.

A well-defined amount of copper may be removed from the sample by passing a current I during time t across the cell so that copper ions migrate in the solid electrolyte toward the copper electrode and electrons are transferred from the $\text{Cu}_{2-\delta}\text{Se}$ sample to the Au electrode. In copper selenide, both ions and electrons are mobile, and therefore, a uniform Cu/Se ratio is readily obtained. The decrease of the Cu/Se ratio, $\Delta\delta$, is

$$\Delta\delta = \frac{q}{nF} = \frac{It}{nF}, \quad (1)$$

where q is the number of coulombs passed across the cell and n is the number of gram-atoms of selenium in the Cu_2Se sample.

3. Results and Discussion

3.1. Ionic Conductivity

A direct current was passed between two silver plates and the potential difference between two Cu/electrolyte reference probes 2 and 4 shown in Fig. 1 was measured. This potential difference increased gradually with time and reached a constant value in a few hours. Ohm's law was established between the current and the steady-state potential difference as shown in Fig. 2, which is a typical example for $\text{Cu}_{1.75}\text{Se}$ measured at 150°C. The ionic conductivity is calculated from the slope of this straight line and the dimensions of the sample. In this way, the ionic conductivities of $\text{Cu}_{1.75}\text{Se}$, $\text{Cu}_{1.90}\text{Se}$, $\text{Cu}_{1.96}\text{Se}$, and $\text{Cu}_{1.99}\text{Se}$ were measured in the temperature range of 30–180°C. The logarithm of the conductivity is plotted against the reciprocal of the absolute temperature in Fig. 3. The ionic conductivities of $\text{Cu}_{1.90}\text{Se}$, $\text{Cu}_{1.96}\text{Se}$, and $\text{Cu}_{1.99}\text{Se}$ show abrupt changes near 110, 85, and 75°C, respectively, which may correspond to the α - β phase transition temperatures of the copper selenides. On the other hand, in the case of $\text{Cu}_{1.75}\text{Se}$, no abrupt change in conductivity is found in the temperature range investigated, showing that no phase transition

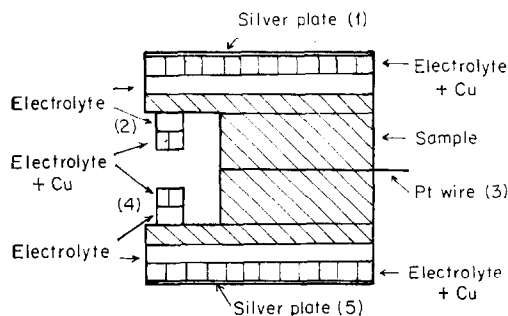


FIG. 1. Arrangement for ionic conductivity measurement cell.

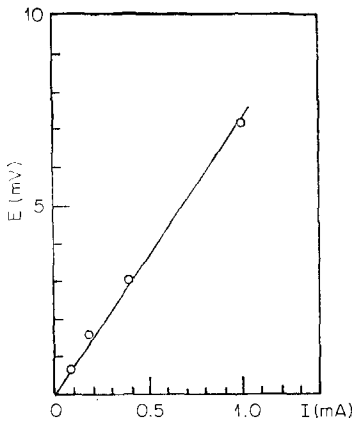


FIG. 2. Steady-state potential difference (E) versus current (I) of the ionic conductivity measurement cell with $\text{Cu}_{1.75}\text{Se}$ at 150°C .

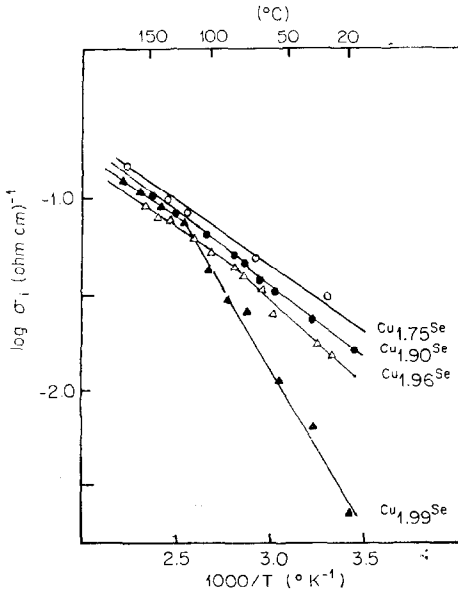


FIG. 3. Ionic conductivities of $\text{Cu}_{2-\delta}\text{Se}$ as a function of temperature.

is observed in this temperature range. The copper ion conductivity of $\text{Cu}_{1.75}\text{Se}$ at room temperature was $3 \times 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$, and the activation energy for ionic conduction was 5.5 kJ/mole , which is comparable to that of high ionic conductivity solids with the so-called average structure (5).

Figure 4 indicates the ionic conductivity of $\text{Cu}_{2-\delta}\text{Se}$ at 150°C as a function of the deviation

tion, δ , from the stoichiometric composition. The stoichiometric composition is assumed here to be realized in the sample equilibrated with pure copper. At this temperature, $\text{Cu}_{2-\delta}\text{Se}$ has α -phase over the whole range of δ investigated. The ratio of Cu/Se was changed by passing a current between the platinum wire electrode 3 and the silver plate 1,5 shown in Fig. 1. The ratio of Cu/Se was calculated from Eq. (1). As shown in Fig. 4, the ionic conductivities decrease linearly as δ increases in the range $0 < \delta < 0.04$.

Copper ion in $\alpha\text{-Cu}_{2-\delta}\text{Se}$, which has an average structure, may be considered to be nearly free to move through a large number of sites within the crystal. In this case, the ionic conductivity, σ_i , is expressed as

$$\sigma_i = en_i u_i \quad (2)$$

where n_i is the concentration of mobile copper ions, u_i is the ionic mobility, and e is the electronic charge. If all coppers in the crystal are ionized and free to move, the relation between n_i and δ may be expressed by

$$n_i = \bar{n}_i - \delta (N_0/V_m) \quad (3)$$

where \bar{n}_i is the concentration of mobile copper ions in the sample equilibrated with pure copper, V_m is the molar volume of Cu_2Se , and N_0 is Avogadro's number. According to the

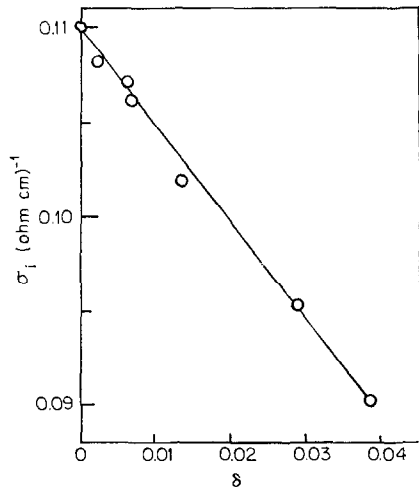


FIG. 4. Ionic conductivity of $\text{Cu}_{2-\delta}\text{Se}$ at 150°C as a function of the deviation from the composition equilibrated with pure copper, δ .

ionic conductivity measurements of the $\text{Ag}_2\text{Se}-\text{Ag}_3\text{PO}_4$ solid solution, which has the average structure similar to $\alpha\text{-Cu}_{2-\delta}\text{Se}$, all the silver ions in the lattice cannot be free to move (5). Therefore, Eq. (3) should be modified as

$$n_i = \bar{n}_i - \beta\delta(N_0/V_m) \quad \text{with } \beta < 1, \quad (4)$$

where β is a constant related to the activity of the copper ions. From (2) and (4), if u_i is independent of n_i near the stoichiometric composition, one has

$$\frac{\sigma_i}{\bar{\sigma}_i} = 1 - \frac{\beta\delta(N_0/V_m)}{\bar{n}_i}, \quad (5)$$

where $\bar{\sigma}_i$ is the ionic conductivity of Cu_2Se . According to this equation, the value of \bar{n}_i/β is determined from the σ_i versus δ curve; one obtains $4.4 \times 10^{21} \text{ cm}^{-3}$ for \bar{n}_i/β . However, unique values of \bar{n}_i and u_i cannot be determined from this curve, but limits are obtained i.e., $\bar{n}_i < 4.4 \times 10^{21} \text{ cm}^{-3}$ and $u_i > 1.5 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{sec}$. The total concentration of copper ion calculated from V_m is $4.0 \times 10^{22} \text{ cm}^{-3}$ in Cu_2Se , which is about ten times larger than this limiting value of \bar{n}_i .

3.2. Coulometric Titration

Figure 5 shows the coulometric titration curves of $\text{Cu}_{2-\delta}\text{Se}$ at 100 and 150°C. A well-defined quantity of charge was passed through the coulometric titration cell and the steady-state open circuit voltage was measured in a few hours. From Eq. (1), δ was calculated.

Figure 5 indicates that at 100°C the cell voltage is constant in the range $0.01 < \delta < 0.05$, and when $\delta > 0.05$, it increases as δ increases. This result suggests that in the range $0.01 < \delta < 0.05$, two phases exist. When $\delta > 0.05$, only a single phase appears at this temperature, that is, $\text{Cu}_{1.95}\text{Se}$ transforms from β -phase to α -phase at 100°C. At 150°C, the cell voltage increases monotonically, that is, $\text{Cu}_{2-\delta}\text{Se}$ has only α -phase over the range of δ investigated.

The temperature dependence of cell voltage gives significant information about the phase transition.

In Fig. 6, an example of the phase diagram of this system is shown. The cell voltage with

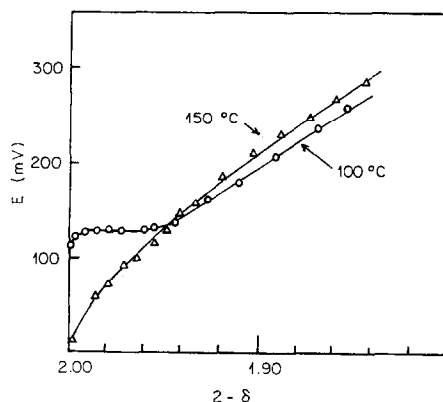


FIG. 5. Coulometric titration curves for copper selenide at 100 and 150°C.

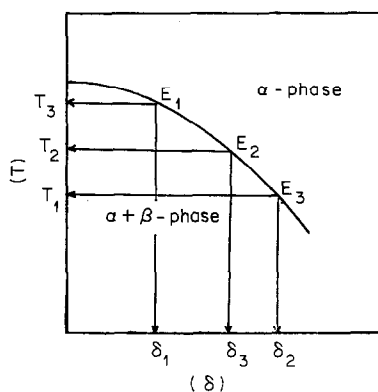


FIG. 6. Model of phase diagram.

$\text{Cu}_{2-\delta_1}\text{Se}$ at T_1 is equal to that with $\text{Cu}_{2-\delta_2}\text{Se}$, E_3 , and at T_2 it is equal to that with $\text{Cu}_{2-\delta_3}\text{Se}$, E_2 . As seen in Fig. 5, the cell voltage increases with increasing δ , and its temperature dependence is not so large. Therefore, the cell voltage decreases with increasing temperature up to T_3 , which is the β - α transition temperature of $\text{Cu}_{2-\delta_1}\text{Se}$. At temperatures higher than T_3 , the cell voltage changes according to the temperature dependence of the chemical potential of copper in this composition.

Figure 7 shows the temperature dependence of voltage of the cell with $\text{Cu}_{2.00}\text{Se}$ and $\text{Cu}_{1.90}\text{Se}$. The minimum values of the cell voltage in both curves appear at a certain temperature which is considered to correspond to the α - β transition point of $\text{Cu}_{2-\delta}\text{Se}$.

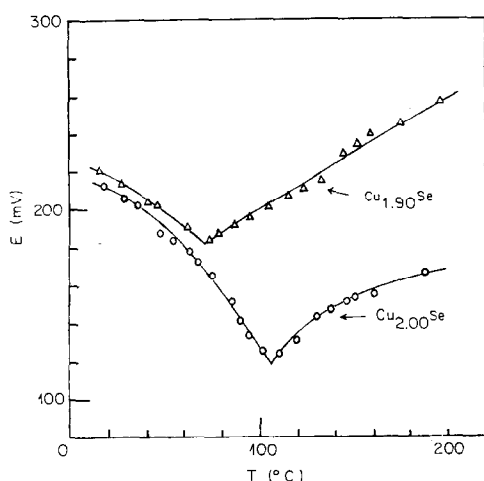


Fig. 7. The cell voltage (E) of the coulometric titration cell for $\text{Cu}_{2.00}\text{Se}$ and $\text{Cu}_{1.90}\text{Se}$ as a function of temperature.

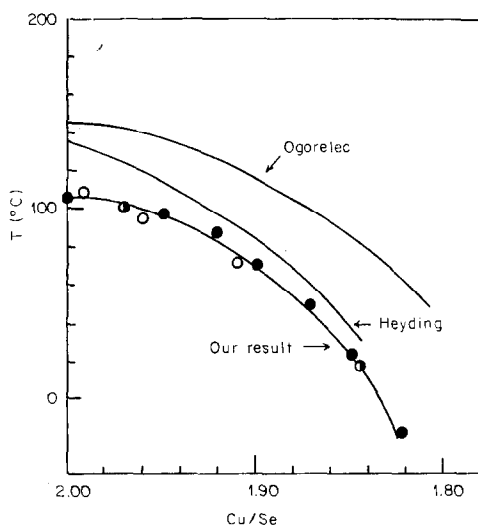


Fig. 8. Phase diagram of copper selenide. ○, obtained from the coulometric titration curves; ●, from the cell voltage versus temperature curves; ○, from the ionic conductivity curves.

From the curves in Fig. 6, the phase transition temperatures are determined to be 106°C for $\text{Cu}_{2.00}\text{Se}$, and 70°C for $\text{Cu}_{1.90}\text{Se}$, respectively. By this method, the transition temperatures of $\text{Cu}_{2-\delta}\text{Se}$ with various δ were obtained for the phase diagram.

3.3. Phase Diagram of Copper Selenide

The β - α transition temperature of $\text{Cu}_{2-\delta}\text{Se}$, which were obtained by coulometric titration and temperature dependence of cell voltage, are plotted as a function of δ in Fig. 8. The transition temperatures deduced from the ionic conductivity measurements are also plotted in Fig. 8. The phase diagrams of this system were reported by Ogorelec (9), Heyding (10), and recently by Koheb (11). Ogorelec investigated the phase diagram by the measurements of electronic conductivity, Heyding by the differential thermal analysis, and Koheb by X-ray diffraction patterns. As shown in Fig. 8, the results obtained by this investigation are somewhat lower than those of Ogorelec or Heyding and nearly similar to those of Koheb.

4. Summary

The ionic conductivity of $\text{Cu}_{2-\delta}\text{Se}$ was measured using the copper ion solid electrolyte. The α -phase was found to have high ionic conductivity even near room temperature. The coulometric titration was carried out to draw the phase diagram of the Cu-Se system in the composition range near Cu/Se = 2.

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