Electronic and Ionic Zeebeck Coefficients in Mixed Conductors of Ag$_{0.25-\delta}$Cu$_{1.75}$Se, Ag$_{1.2-\delta}$Cu$_{0.8}$Se$^1$

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Abstract—The paper presents the studies of ionic and electronic Zeebeck coefficients and electronic conductivity in nonstoichiometric Ag$_{0.25-\delta}$Cu$_{1.75}$Se, Ag$_{1.2-\delta}$Cu$_{0.8}$Se solid solutions existing on the basis of the cubic phase of copper selenide. It is shown that Ag$_{1.2-\delta}$Cu$_{0.8}$Se is a bilateral variable composition phase manifesting inversion of the sign of predominant charge carriers under variation of the chemical composition by silver within the homogeneity region. Mobilities of electrons and electron holes are estimated on the basis of the concentration dependences.

Keywords: homogeneity region, coulometric titration, carrier mobility, thermoelectric materials, ionic thermo-EMF, electronic thermo-EMF

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INTRODUCTION

Studies of kinetic phenomena in mixed electronic-ionic conductors of the Cu$_2$Se–Ag$_2$Se quasibinary system are of interest both from the fundamental point of view [1] and in connection with the prospects of using these alloys in thermoelectric [2–5] and photoelectric devices [6, 7].

Solid solutions of the Cu$_2$Se–Ag$_2$Se system were studied by a number of authors [8–11]. Solid solutions of Cu$_2$Se–Ag$_2$Se have extremely high for solids self-diffusion coefficients of cations ($10^{-5}$ cm$^2$ s$^{-1}$) and chemical diffusion coefficients (up to $10^{-2}$ cm$^2$ s$^{-1}$) [12]. In addition to unusually high ion transport parameters, these materials are of considerable interest for semiconductor electronics in connection with the possibility of easy tuning of electronic properties by varying their nonstoichiometricity degree by electrochemical methods [1, 9]; with application of nanotechnologies, these possibilities are much enhanced (see, e.g., [13, 14]).

The region of solid solubility in the system of Ag$_2$Se–Cu$_2$Se was studied using X-ray diffraction methods in [15]. It was found that a mixture of phases of Cu$_2$–Se, AgCu$_2$Se, and Ag$_2$Se is formed at the temperatures of 20–180°C; below 180°C, AgCu$_2$Se has a tetragonal system; above 200°C, the existing solutions are quasibinary solid solutions Cu$_x$Ag$_{2-x}$Se based on the Ag$_2$Se phase with a body–centered cubic lattice (from Ag$_2$Se to Ag$_{1.5}$Cu$_{0.5}$Se) and solid solutions based on the Cu$_2$Se phase with a face-centered cubic lattice (fcc phases) (from Cu$_2$Se to Cu$_{0.7}$Ag$_{1.3}$Se). The polymorphous transition occurs at 130°C in Cu$_2$Se and at 133°C in Ag$_2$Se [16]. There is the eucairite mineral with the approximate chemical formula of AgCu$_2$Se [17]. There are also natural sulfide crystals with the approximate composition of Ag$_{1.25}$Cu$_{0.75}$S: mckinstryite. However, there is no information in the literature about a crystal similar to mckinstryite, selenide (with the formula of Ag$_{1.25}$Cu$_{0.75}$Se or Ag$_{1.2}$Cu$_{0.8}$Se) [18].

The known publications on electronic transfer in the Ag$_2$Se–Cu$_2$Se system are mostly those of Z. Ogorelec, S. Miyatani, V. Berezin et al. [1, 9, 19–21]. They found that solid solutions based on Cu$_2$Se exist with metal deficiency in the metallic sublattice and are characterized by $p$-type semiconductor conductivity. At the content of Ag$_2$Se in the solid solution above 30 mol %, a narrow homogeneity region with metal excess with respect to the stoichiometric composition with $n$-type conductivity appears, due to which an inversion of the conductivity type occurs within the homogeneity region of such solutions as a result of variation of the nonstoichiometricity degree.

The aim of this work was to study the temperature and composition dependences of the coefficients of thermo-EMF and electronic conductivity in berthol-
lide and daltonide nonstoichiometric phases of solid solutions of $\text{Ag}_{0.23-\delta}\text{Cu}_{1.75}\text{Se}$ and $\text{Ag}_{1.2-\delta}\text{Cu}_{0.8}\text{Se}$ existing on the basis of the fcc phase of copper selenide.

**EXPERIMENTAL PROCEDURE**

**Technique of Coulometric Titration**

Application of this method allows studying concentration dependences of physical properties of the variable composition superionic phase using a single sample, which is a substantial convenience for the researcher. The coulometric titration technique is based on the application of the electrochemical cell of the following type:

$$\text{Pt} | \text{AgI} | \text{Ag}_{2+\delta}\text{Se} | \text{Pt},$$

(1)

where $\text{AgI}$ is a unipolar ionic conductor by Ag ions, $\text{Ag}_{2+\delta}\text{Se}$ is a sample, instead of which any silver-conducting electron–ion conductor with a homogeneity region (or an intercalate, e.g., TiS$_2$) can be used. The theory of the method was developed by C. Wagner [22]. Wagner obtained an expression for EMF of electrochemical cell (1) appearing between two platinum contacts of cell (1) with account for the fact that diffusion in a mixed electron-ion conductor occurs much faster than in the electrolyte:

$$E = -\left(\frac{\mu_{\text{Ag}} - \mu_{\text{Ag}}^0}{e}\right),$$

(1)

where $\mu_{\text{Ag}}$ is the chemical potential of a silver atom in the sample, $\mu_{\text{Ag}}^0$ is the chemical potential of a silver atom in metallic silver.

Equation (1) shows that EMF $E$ of cell (1) can be used to determine the variation of the chemical potential of silver atoms in the sample and therefore variation of silver content in the $\text{Ag}_{2+\delta}\text{Se}$ phase.

Sample composition, i.e., the metal/chalcogen ratio can be measured with a high degree of accuracy within the homogeneity region of the compound using the electrochemical method with application of direct current to the type (1) cell. Owing to application of the ionic filter, there is not only ionic current in the circuit and the charge passing through the cell is a measure of variation of sample composition (transport numbers of anions can be neglected).

Variation of stoichiometric phase index $\Delta\delta$ can be determined from Faraday’s law of electrolysis:

$$\Delta\delta = \frac{I\Delta t}{n_xF},$$

(2)

where $n_x$ is the number of gram-atoms of the chalcogen in the sample; $I$ is the current, $\Delta t$ is the time of application of current.

This method is characterized by high accuracy: the minimum change in the composition that can as yet be sufficiently reliably controlled is $\Delta\delta = 10^{-8}$ in the formula $\text{Me}_{2-\delta}\text{X}$.

The dependence of EMF $E$ of the electrochemical cell of type (1) on nonstoichiometricity degree $\delta$ is the coulometric titration curve. The $E(\delta)$-curves measured in advance are used for determination of the unknown value of $\delta$ on the basis of the measured value of $E$ and can also be used for determination of the width of the homogeneity region [23], phase formation potentials, effective mass of electronic carriers [24], thermodynamic parameters of the compounds [24, 25] etc.

Owing to the strong disordering of the cationic sublattice of the studied objects, the chemical potential of silver ions weakly depends on variation of the silver concentration within the homogeneity region, so that according to formula (1) EMF of the electrochemical cell is determined only by variation of the chemical potential of electrons, thus, corresponding to the height of the Fermi level in the sample vs. the Fermi level in the silver electrode [1, 12]. This allowed studying the properties of these materials as dependent on the position of the Fermi level.

**Preparation and Characterization of Samples**

The alloys were manufactured by sintering of powders of binary copper and silver selenides at the corresponding weight ratios. The synthesis was carried out in evacuated quartz ampoules, at the residual pressure of $\sim 10^{-3}$ Pa at the temperature of 500°C for 72 h. Measurement samples have the shape of a parallelepiped with the size of $3 \times 0.5 \times 0.2$ cm$^3$.

The phase composition of the obtained samples was studied using X-ray diffractometry at a DRON-4 diffractometer (Russia) using $K_\alpha$ copper radiation. Figure 1 shows the diffraction pattern of the $\text{Ag}_{0.2}\text{Cu}_{1.8}\text{Se}$ sample obtained at the room temperature. The diffraction pattern contains the lines of $\text{Cu}_2\text{Se}$, $\text{AgCuSe}$, and $\text{Ag}_2\text{Se}$.

![Fig. 1. Diffraction pattern of the $\text{Ag}_{0.2}\text{Cu}_{1.8}\text{Se}$ sample obtained at the room temperature.](image-url)