

Effect of lithium doping on electrophysical and diffusion proper-ties of nonstoichiometric superionic copper selenide $\text{Cu}_{1.75}\text{Se}$

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The results of studies of the ionic conductivity and the conjugated chemical diffusion coefficients (CCDC) in the nonstoichiometric $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($0 \leq x \leq 0.25$) ternary alloys are presented. It has been observed that the values of the ionic conductivity of $\text{Cu}_{1.75}\text{Se}$ copper selenide decreases with lithium doping in general owing to increasing the activation energy. The increasing of the conjugate chemical diffusion coefficients of the cations and electron holes was observed with increasing of lithium content, despite the decreasing of self-diffusion coefficients of the cations and decreasing of electron mobilities. The behavior of the conjugate chemical diffusion coefficients explained by a decrease in the degree of non-stoichiometry of the composition, leading to an increase of the internal electric field accelerating the motion of slower particles.

Keywords: superionic conductors, diffusion, conductivity, copper selenide.

Introduction

Copper selenide is a well-known superionic conductor with mixed electron-ion conductivity. The great variety of interesting physical properties, many of which have perspectives of practical application, has made this material an object of intensive studies in recent decades. It can be noted such applications as superionic conductors [1, 2], ion-exchange materials for the synthesis of nanocrystals [3], solar cells [4], thermoelectricity [5-6], batteries [7, 8], gas sensors [9], optical devices (surface plasmon resonance) [10, 11], quantum dots for lasers and LEDs [12], medical devices [13-14], etc.

Copper selenide exhibits high ionic conductivity (up to 3 S/cm) simultaneously with the pre-dominant electronic conductivity of the p-type ($10^2 - 10^3$ S/cm). The electronic conductivity, Seebeck coefficient and other electrical properties of copper selenide strongly depend on the non-stoichiometry of the composition [15-17]. At 137°C the phase transition occurs in Cu_2Se from the low-symmetry β - phase to the cubic α -phase, which demonstrates a high mobility of the cations. The strong disordering of the cation sublattice in α -phase

creates favorable conditions for the high ionic conductivity, the large width of the homogeneity region, and low lattice thermal conductivity. Elements of structural disordering are also retained in the low-temperature β -phase of copper selenide.

Concern to the crystal structure of the copper selenide β -phase, there are many disagreements in the literature. Tetragonal, monoclinic, pseudo-orthorhombic, triclinic syngonies have been attributed to it [18], the tendency of copper atoms in the low-temperature phase to order with the formation of superstructures [19-20]. The unit cell of the low-temperature phase can be described as a distorted cube of the high-temperature phase deformed along a large diagonale.

In recent years copper selenide has been intensively studied owing to the increased interest in its thermoelectric properties. The excellent thermoelectric properties of copper and silver chalcogenides have long been known [21-23], but their practical application is hampered by the high diffusion rate of copper: at elevated temperatures, rapid degradation of thermoelements occurs due to the extraction of copper. For this reason, in the 80's years of the 20th century, the development of thermoelectric devices with silver-doped copper selenide was curtailed [24], some problems were described in [25, 26] too. The boom of interest in this class of materials revived after the publication of the article [27], in which an emphasis was placed on the superionic, "liquid-like" crystal nature of copper selenide, contributing to the reduction of lattice thermal conductivity (the "phonon glass" effect [28]). So a new trend was created in the search for effective thermoelectrics among the super-ionic materials [29].

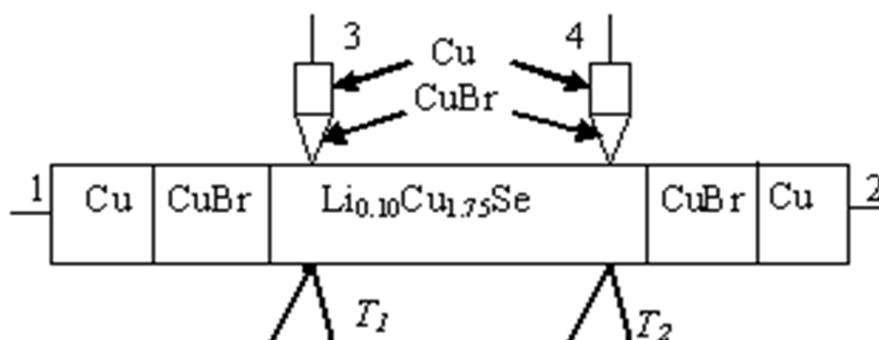


Figure 1. Scheme of the electrochemical cell for measurements of the ionic DC conductivity and the chemical diffusion coefficients.

Over the past 3-4 years of intensive research, the dimensionless thermoelectric figure of merit $ZT = \alpha^2 \sigma T / k$ was increased for copper selenide (prepared in a ball mill) to 2.1 at 700 K [30]. The main reason for such high ZT is believed to be a result of the enhancement of low-to-high wave-length phonon scatterings by various defects of the wide range of nano- to meso-scale dimensions which are formed during ball milling process. However, high ionic conductivity and high probability of a rapid degradation of the device, call into question the advisability of further improving of thermoelectric properties of the superionic materials [31]. The problem of degradation can be solved by the ionic conductivity decreasing with optimal alloying of the material.

We previously studied the substitution of copper by lithium in copper selenide in the $\text{Li}_x\text{Cu}_{2-x}\text{Se}$ ($0 \leq x \leq 0.25$) compositions, which were prepared by doping non-stoichiometric Cu_{2-x}Se phases with the amount of lithium so that

the total cation content was the same as in stoichiometric Cu_2Se . Substitution by lithium revealed a significant decrease in both the ionic and the electronic conductivity, a decrease of the self-diffusion coefficients of cations and the chemical diffusion coefficients [32-36], while maintaining and even increasing the electronic Seebeck coefficient were observed.

An increase in the stability of the chemical composition of copper selenide at lithium doping was reported in a recent paper by S. D. Kang et al. [37], they obtained the high value of $ZT = 1.4$ for the $\text{Li}_{0.09}\text{Cu}_{1.9}\text{Se}$ composition at 727°C .

In this paper, we report the results of investigations of ionic and electronic conductivity, chemical diffusion coefficients for $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($0 \leq x \leq 0.25$) compositions with a deficiency of cations in the crystal lattice. From the point of view of thermoelectric applications, such substitution should be promising, since with decreasing ionic conductivity, the electronic conductivity will remain high owing to the large concentration of vacancies in the cation sublattice.

Experimental methods

Samples $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($0 \leq x \leq 0.25$) were synthesized by solid-phase reaction of $\text{Cu}_{1.75}\text{Se}$ powder with the corresponding amount of metallic lithium with a stepwise increase of the annealing temperature from room temperature to 400°C during the week. Homogenization annealing was carried out at 400°C for 100 hours. The phase content of the samples was studied by X-ray diffraction analysis using a DRON-3.0 diffractometer (Russia). Samples for measurements in the form of parallelepipeds with dimensions of $20 \times 5 \times 3 \text{ mm}^3$ were obtained by cold pressing at a pressure of 300-500 MPa. The grain sizes of the samples according to the optical and electronic microscopy data were 80-100 μm . The ionic conductivity was measured by the direct current method at suppressing of the electronic component of the current [38], the circuit of the measuring cell is shown in Figure 1. Electrodes from a suitable solid electrolyte with unipolar Cu^+ ionic conductivity in the necessary temperature range ($\text{Cu}_4\text{RbCl}_3\text{I}_2$, CuBr , CuI) were used to block the electronic current component. The stationary potential difference V_{ii} measured between two ionic probes of the $\text{Cu}|\text{CuBr}$ type (contacts 3, 4 in Figure 1) at the passage of a low-density direct current through the sample (contacts 1 and 2 of the cell) makes it possible to determine the value σ_i of the ionic conductivity. Under the condition that only copper ions can pass through ion filters ($\text{Cu}_4\text{RbCl}_3\text{I}_2$, or CuBr or CuI), and lithium ions are blocked, the applied measurement method determines the value of the total ionic conductivity accordingly to the theory developed by Miyatani [39]. Taking into account the dependence of the ionic conductivity, chemical diffusion coefficient, and electronic conductivity on grain sizes [35, 40, 41], these measurements were carried out on coarse-grained samples with an average grain size of 80-100 μm .

The time dependence of the potential difference $V_i^i(t)$ is related with the processes of establishing and decay of the concentration polarization in the sample and makes possible to find the coefficient \tilde{D} of conjugate chemical diffusion from the relation

$$V_i^i(t) = V_i^i(0) \exp(-\pi^2 \tilde{D} t / L^2), \quad (1)$$

where $V_i^i(0)$ is the ionic potential difference at the instant of current switching off, L is the length of the sample [38]. All measurements were carried out in an inert atmosphere of dry purified argon.

Results and discussion

Ionic conductivity and chemical diffusion. Figure 2 shows the temperature dependences of the ionic conductivity (σ_i) of five samples of the $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ system ($x = 0.05, 0.10, 0.15, 0.20$ and 0.25) and, for comparison, two binary compositions (Cu_2Se and $\text{Cu}_{1.75}\text{Se}$). From Figure 2, the highest ionic conductivity is shown by Cu_2Se copper selenide, and the lowest one is observed for $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$, so, in general, doping with lithium leads to a decreasing of the ionic conductivity. It was previously established that lithium ions overlap the light diffusion pathways of copper ions in copper selenide, decreasing ionic conductivity [33, 34]. The non-stoichiometry degree of the composition must also be taken into account, since it is known that the ionic conductivity of $\text{Cu}_{2-\sigma}\text{Se}$ decreases with non-stoichiometry degree σ increasing [17], followed by decreasing the concentration of mobile copper ions. Lithium ions in $\text{Li}_x\text{Cu}_{1.75}\text{Se}$, in our opinion, are also mobile, since Li_2Se has a similar with Cu_2Se the FCC structure of the Fm3m type with close unit cell parameters and exhibits superionic conductivity at elevated temperatures [42]. When the lithium content in $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ increases, the concentration of mobile ions increases too, which should increase the ionic conductivity, but the mobility of lithium ions is apparently lower than the mobility of copper ions; therefore, the ionic conductivity of the $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ compounds should be lower than those of binary copper selenides $\text{Cu}_{2-\sigma}\text{Se}$ with the same cation deficiency in the lattice ($\sigma = 0.25-x$), and, in any case, lower than those in Cu_2Se .

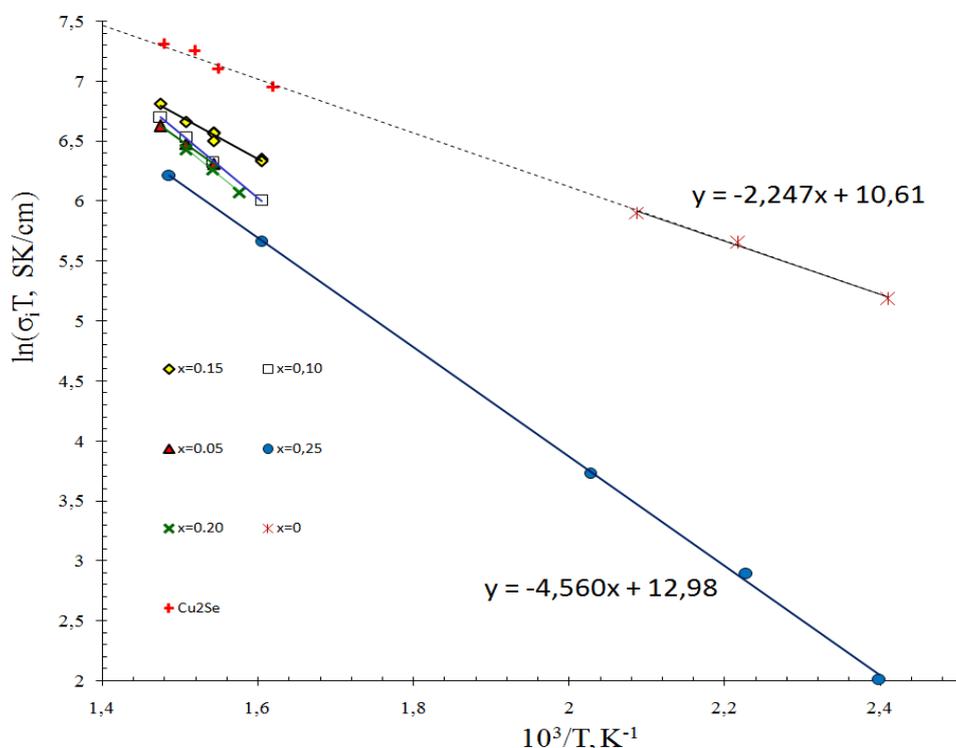


Figure 2. The temperature dependences of the ionic conductivity of the $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($x = 0, 0.05, 0.10, 0.15, 0.20$ and 0.25) and Cu_2Se samples.

Table 1 contains the ionic conductivity values of the samples at temperatures close to 400°C , as well as the activation energies of the ionic conductivity, determined from the slope of the $\ln(\sigma_i)(1/T)$ lines in Figure 2. In lithium-doped

copper selenides, the activation energy values of the ionic conductivity is much higher than those in binary compositions, and it indicates a serious change in the potential lattice relief at doping with lithium: the relief becomes "deeper".

Table 1.

Parameters of ionic transport for Cu_{2-x}Se and $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ alloys.

Composition	$T^\circ\text{C}$	$\sigma_i, \text{S/cm}$	$\tilde{D}, 10^3\text{cm}^2/\text{s}$	E_a, eV	\tilde{E}_a, eV
Cu_2Se	403	2.02 ± 0.08	3.5	0.21 ± 0.02	-
$\text{Cu}_{1.75}\text{Se}$	206	0.76 ± 0.04	0.28	0.19 ± 0.02	0.25 ± 0.03
$\text{Li}_{0.05}\text{Cu}_{1.75}\text{Se}$	405	1.11 ± 0.04	0.38	0.40 ± 0.04	0.50 ± 0.05
$\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}$	405	1.19 ± 0.04	0.46	0.46 ± 0.04	0.61 ± 0.05
$\text{Li}_{0.15}\text{Cu}_{1.75}\text{Se}$	390	1.34 ± 0.05	0.54	0.30 ± 0.03	0.34 ± 0.03
$\text{Li}_{0.20}\text{Cu}_{1.75}\text{Se}$	390	0.93 ± 0.04	0.58	0.45 ± 0.04	-
$\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$	405	0.74 ± 0.03	0.67	0.39 ± 0.03	0.36 ± 0.03

It is necessary to study the crystal structure and cation distribution between interstitial sites for the $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ alloys in order to draw a detailed picture of the effect of lithium doping on the ionic transport, since similar studies for $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ revealed that when lithium copper selenide is doped with lithium, a tendency appears to some ordering of the lattice and to shifting of the phase transition point into a cubic modification toward higher temperatures. Binary copper selenide $\text{Cu}_{1.75}\text{Se}$ has a cubic lattice at room temperature already and is a superionic conductor, while $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ lattice has a triclinic syngony at room temperature and reaches cubic symmetry only at 437°C , across phase transitions with symmetry increasing at 137°C (to the monoclinic phase), 237°C (to the rhombohedral phase), 377°C (to the hexagonal phase) [33].

Figure 3 shows the temperature dependences of the coefficient of the conjugate chemical diffusion (CCDC) of cations and electrons in $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($x = 0.05, 0.10, 0.15, 0.25$) alloys. It can be seen that the above mentioned dependences demonstrate Arrhenius character. Table 1 contains the CCDC values of samples at temperatures close to 400°C , as well as values of the activation energy of chemical diffusion, determined from the slope of the $\ln(1/T)$ lines in Figure 3.

It is known that in copper selenide $\text{Cu}_{2-\sigma}\text{Se}$, the CCDC decreases monotonically with increasing of deviation σ from the stoichiometric composition [17]. High values of the chemical diffusion coefficient are explained both by a high self-diffusion coefficient of cations ($\sim 10^{-5}\text{cm}^2/\text{s}$) and by the appearance of an internal electric field in the electron-ion conductor accelerating the diffusion of "slow" particles-cations [43]. In the $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ alloys, the CCDC is much lower than those in Cu_2Se , but higher than CCDC in $\text{Cu}_{1.75}\text{Se}$. With increasing x in the formula $\text{Li}_x\text{Cu}_{1.75}\text{Se}$, the CCDC increases, since the deficit $\sigma' = 0.25 - x$ of cations in the lattice decreases – by another words, the same mechanism as in the binary copper selenide continues to operate. However, for $\sigma' = 0$ (corresponding to $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ composition), CCDC is still considerably less than those in Cu_2Se . This may be a consequence of the fact that both the self-diffusion coefficient of cations and the mobility of electrons in $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ are lower than in Cu_2Se . The values of activation energies of the ionic conductivity for "non-stoichiometric" $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ alloys, as can be seen from Table 1, are close to the

corresponding values of activation energy of chemical diffusion, what was noted earlier for "stoichiometric" $\text{Li}_x\text{Cu}_{2-x}\text{Se}$ alloys [32].

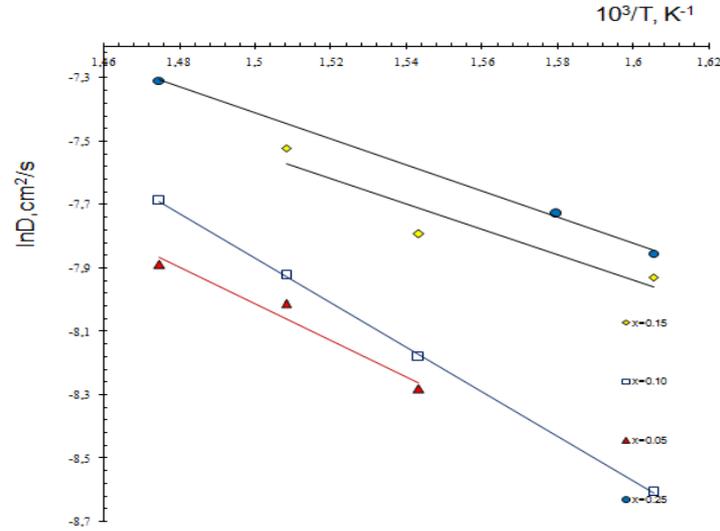


Figure 3. The temperature dependences of the conjugate chemical diffusion coefficient of cations and electrons in $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($x = 0.05, 0.10, 0.15, 0.25$) alloys.

The Fermi energy and the entropy of the metal atoms in $\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}$

Figure 4 shows the temperature dependence of the e.m.f. E of electrochemical $\text{Cu}/\text{CuI}/\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}/\text{C}$ cell. In mixed electron-ion conductors with strongly disordered crystal structure, the eE value of the similar cell equals to the difference between the Fermi level of electrons in the sample and the metal electrode (copper in our case), assuming the chemical potential of mobile ions remains unchanged [44]:

$$\mu = \mu_{\text{Cu}}^0 + eE. \quad (2)$$

Derivative $\delta E/\delta T$ gives information on the entropy of atoms in the lattice [45]:

$$S_{\text{Cu}} - S_{\text{Cu}}^0 = e \frac{\delta E}{\delta T}. \quad (3)$$

A break in the $E(T)$ dependence at about 440 °C may indicate structural changes (note that in $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ there is a transition to the cubic modification at 437 °C). Above 490 °C, the entropy of copper atoms in $\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}$ ceases to change, which can be interpreted as the completion of structural transformations.

Electronic conductivity. $\text{Cu}_{2-\sigma}\text{Se}$ can be considered as a semiconductor with impurity conductivity, in which vacancies in the cation sublattice serve as acceptors. The limiting impurity concentration corresponds to the edge of the homogeneity region of the phase ($\sigma = 0.25$), and at that strong concentration the acceptor levels of the Cu^{2+} "impurities" can be associated into an impurity band. The width of the band gap of Cu_2Se is $E_g = 1.25$ eV according to [21], the optical width of the band gap depends on the copper content in the phase and is 1.1, 1.6 and 1.7 eV for Cu_2Se , $\text{Cu}_{1.84}\text{Se}$, and $\text{Cu}_{1.82}\text{Se}$, respectively [46]. At high temperatures in $\text{Cu}_{2-\sigma}\text{Se}$, the average free path of holes does not exceed the lattice period [47].

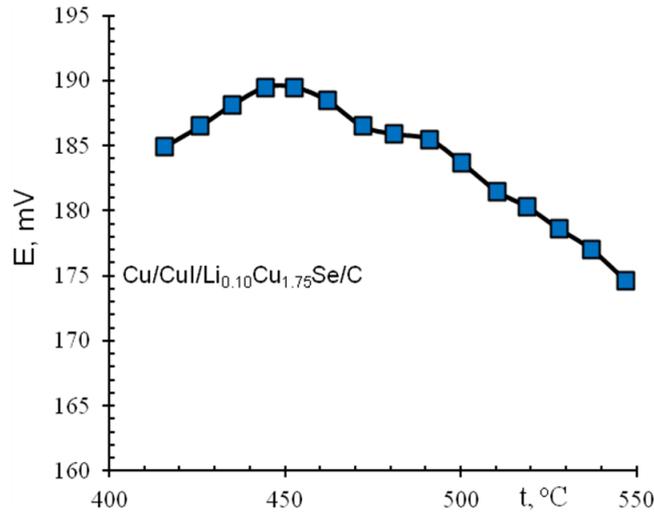


Figure 4. The temperature dependence of the e.m.f. of electrochemical Cu/Cu/Li_{0.10}Cu_{1.75}Se /C cell.

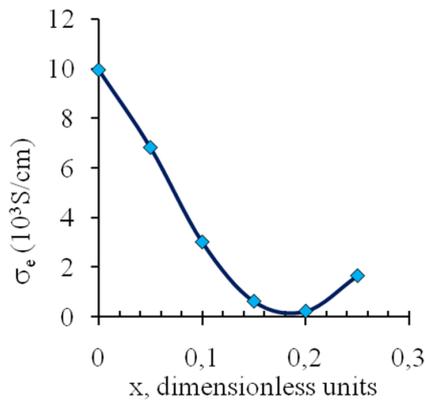


Figure 5. Dependence of the electronic conductivity on the lithium content x for $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ samples at room temperature (from paper [36]).

Lithium most likely acting as monovalent donor impurity at the substitution of copper $\text{Cu}_{2-\sigma}\text{Se}$, and thus, $\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}$ compositions must be partially compensated semiconductors, and the composition $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ must be fully compensated semiconductor.

Figure 5 shows a plot of electronic conductivity $\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}$ samples versus lithium content at room temperature from our earlier work [36]. In Figure 5, the conductivity decreases substantially lin-early to a content $x \approx 0.15$, which can be attributed to a decrease in the hole concentration, as a total metal composition approaches to stoichiometric composition, and accordingly concentration of the vacancies in the cation sublattice decreases. A solid solution is formed, which is confirmed by a monotonic change of the lattice parameter.

The change in the character of the dependence in Figure 5 at $x \geq 0.17$ may be due to a change in the mechanism of defect formation. Studies using coulometric titration have shown that non-stoichiometric copper selenide is capable to dissolve lithium more than copper. Copper selenide exists only with a deficit of metal with respect to the stoichiometric composition, but the $\text{Li}_y\text{Cu}_{2-x}\text{Se}$ alloys can exist also with an excess of metal ($y \geq x$), i.e. they have a two-sided region of homogeneity, which leads to the appearance of a minimum on the dependence of the conductivity on the metal content.

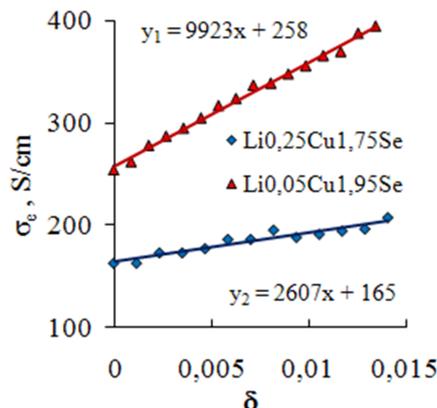


Figure 6. The electronic conductivities of $\text{Li}_{0.05}\text{Cu}_{1.93+\sigma}\text{Se}$ and $\text{Li}_{0.25}\text{Cu}_{1.73+\sigma}\text{Se}$ samples as functions of the content of injected copper in the initial compositions ($\text{Li}_{0.05}\text{Cu}_{1.93}\text{Se}$ and $\text{Li}_{0.25}\text{Cu}_{1.73}\text{Se}$) at 350 °C.

The lithium content in the alloy affects the conductivity, lowering the carrier mobility, and possibly lowering their concentration. This can be seen in Figure 6, which shows the electronic conductivity of $\text{Li}_{0.05}\text{Cu}_{1.93+\sigma}\text{Se}$ and $\text{Li}_{0.25}\text{Cu}_{1.73+\sigma}\text{Se}$ samples as a function of the content of injected copper in the initial compositions ($\text{Li}_{0.05}\text{Cu}_{1.93+\sigma}\text{Se}$ and $\text{Li}_{0.25}\text{Cu}_{1.73+\sigma}\text{Se}$) at 350 °C. The conductivity of $\text{Li}_{0.25}\text{Cu}_{1.73+\sigma}\text{Se}$ is lower by a factor of 1.5-2, whereas the carrier mobility is lower by almost 5 times ($5 \text{ cm}^2 / \text{V s}$ for $\text{Li}_{0.25}\text{Cu}_{1.93+\sigma}\text{Se}$ versus $1.2 \text{ cm}^2 / \text{V s}$ for $\text{Li}_{0.25}\text{Cu}_{1.73+\sigma}\text{Se}$). The hole mobility was estimated from the $\sigma_e(\delta)$ dependence according to the approximate formula $\mu_p \approx Vm / [F (d\sigma / d\delta)]$, where Vm is the molar volume of the phase, $F = 96480 \text{ Ql/mol}$ is the Faraday constant.

In Figure 7 the dependence of the electronic conductivity $\sigma_e(E)$ of the $\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}$ sample on the e.m.f. E of $\text{Cu/CuI/Li}_{0.10}\text{Cu}_{1.75}\text{Se/C}$ cell is presented in the temperature range 410-550 °C. The $E(T)$ dependences (Figure 4) and $\sigma_e(E)$ were recorded simultaneously with the same sample during the measurement of the temperature dependence of the electronic conductivity. Figure 7 shows that the conductivity almost linearly depends on the cell e.m.f. E , which is the relative height of the Fermi level of the electrons. The break in the $\sigma_e(E)$ curve at $E \approx 190 \text{ mV}$ corresponds to a kink on the $E(T)$ curve at 450 °C, and is apparently related with structural transformation near this temperature.

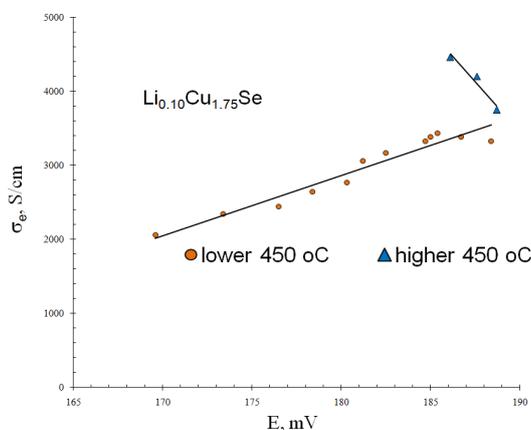


Figure 7. The dependence of the electronic conductivity of $\text{Li}_{0.10}\text{Cu}_{1.75}\text{Se}$ sample on the e.m.f. E of $\text{Cu/CuI/Li}_{0.10}\text{Cu}_{1.75}\text{Se/C}$ cell in the temperature range 410-550 °C.

Conclusion

From measurements of the ionic conductivity and chemical diffusion coefficients (CCDC) in nonstoichiometric $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($0 \leq x \leq 0.25$) ternary alloys, it can be seen that lithium doping reduces the values of total ionic conductivity of copper selenide $\text{Cu}_{1.75}\text{Se}$, and it is associated with the increase in the corresponding activation energy. In connection with the prospects of copper selenide using in thermoelectric devices, this is a positive moment, as it reduces the risk of degradation of thermoelements during operation.

There is also a significant decrease in the mobility of electron carriers with increasing of the lithium content, but the level of electron conduction can be high at the same time due to the control of the nonstoichiometry of the composition.

The observed increase of the coefficients of the conjugate chemical diffusion of cations and electrons at an increasing of the lithium content in $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ ($0 \leq x \leq 0.25$) can be explained by the competition of two factors: a reduction in cation mobility with an increasing of the x content of impurities and a decreasing of the nonstoichiometry degree of the composition (vacancy concentration in the cationic sublattice), which determines the accelerating effect of the internal electric field on the diffusion of slower particles (cations). An CCDC maximum is achieved in the binary copper selenide $\text{Cu}_{2-\sigma}\text{Se}$ at stoichiometric composition ($\sigma = 0$). The magnitude of the total non-stoichiometry of the composition (the difference between the stoichiometric value=2 for monovalent monovalent copper and lithium and the sum ($x + 1.75$) of the stoichiometric indices of lithium and copper) affects the CCDC more strongly than the growth of the impurity concentration.

It is necessary to study the crystal structure and the phase diagram of the $\text{Li}_x\text{Cu}_{1.75}\text{Se}$ alloys in order to obtain a more detailed picture of the effect of lithium doping on the ionic and electronic transport, since similar studies for $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ showed that when lithium copper selenide is doped with lithium, a tendency appears to some ordering of the lattice and to the shift of the phase transition point into a cubic modification toward higher temperatures.

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