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Phase Transformations and Ionic Transport in the $Cu_{2-\delta}Te$ Superionic Conductor

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Results are presented for the structural features of $Cu_{2-\delta}Te$ and the ionic transport as a function of temperature and nonstoichiometricity degree in the interval $T = 20$ to 450 °C and $\delta = 0$ to 0.08. The phase transformations are shown to be first-order phase transitions accompanied by changing the activation energy for ionic conduction. The ionic conductivity at 400 °C equals 0.8 Ω^{-1} cm^{-1} and decreases with deviation from stoichiometry. The chemical diffusion coefficient decreases from 8×10^{-4} cm^2 s^{-1} to 4.4×10^{-4} cm^2 s^{-1} when δ changes from 0.015 to 0.075 and $T = 400$ °C. The phase transition is also found in the anomalous dependence of the ionic thermo-e.m.f. on temperature. The ionic transport heat, as calculated from the ionic thermo-e.m.f., equals 0.23 at $\delta =$ = 0.015.

Представлены результаты исследований структурных особенностей $Cu_{2-\delta}Te$ и явлений ионного переноса как функция температуры и степени нестехиометричности в интервале $T = 20$ до 450 °C и $\delta = 0$ до 0,08. Показано, что фазовые переходы являются переходами 1-го рода и сопровождаются изменением энергии активации ионной проводимости. Ионная проводимость равна 0,8 Ω^{-1} cm^{-1} при 400 °C и уменьшается с отклонением от стехиометрии. Коэффициент химической диффузии уменьшается с 8×10^{-4} cm^2 s^{-1} до $4{,}4 \times 10^{-4}$ cm^2 s^{-1} при изменении δ с 0,015 до 0,075 и $T = 400$ °C. Фазовый переход обнаруживается также в аномальной зависимости ионной термо-э.д.с. от температуры. Теплота переноса ионов, расчитанная исходя из ионной термо-э.д.с., равна 0,23 eV при $\delta = 0{,}015$.

1. Introduction

Copper telluride is a compound of variable composition with copper deficit [1]. The homogeneity region of $Cu_{2-\delta}Te$ reaches $\delta = 0.08$ at 400 °C [2]. With increasing temperature $Cu_{2-\delta}Te$ undergoes a number of phase transformations at 305, 360, and 555 °C [3]. Being a p-type degenerated semiconductor in its electrical properties copper telluride exhibits an anomalously high cation conductivity. Estimated from the build-up and decay curves of the concentration polarization, the ionic conductivity is equal to 30 Ω^{-1} cm^{-1} [4]. The present paper shows the results of investigations of the structural transformations in $Cu_{2-\delta}Te$ and the ionic transport features in the range 325 to 450 °C as a function of the degree of non-stoichiometry.

2. Experimental Technique

Using the ampoule-synthesis method, the specimens for the investigations were prepared from elements of exceptional purity by coagulating them in a vacuum at 600 °C with subsequent homogenization at 400 °C. The specimens were single-phase

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as was controlled by X-ray analysis. Powder diffractograms were taken by means of a diffractometer having a high-temperature attachment with CuK_α radiation using a β-filter. The recording of the diffraction line profile to estimate the lattice parameters was made at steps of 0.025°. The measuring temperature was kept constant with a precision to ± 0.5 K.

The ionic conductivity, the chemical diffusion coefficient, and the ionic thermo-e.m.f. of the single-phase specimens were studied with the help of a cell of type (i)

$$\begin{array}{l} \mathrm{Pt_1} \mid \mathrm{Cu} \mid \mathrm{CuBr} \mid \mathrm{Cu_{2-\delta}Te} \mid \mathrm{CuBr} \mid \mathrm{Cu} \mid \mathrm{Pt_4}\,. \\ \mathrm{Pt_2} \text{———————}\!\uparrow \qquad \uparrow\!\text{———————}\ \mathrm{Pt_3} \end{array}$$

The use of CuBr having a unipolar copper ion conductivity in the temperature range 300 to 450 °C [5] allows only the ionic current to pass through the $\mathrm{Cu_{2-\delta}Te}$ specimen studied. Stationary values of the potential difference V_i^i between two potential probes Cu/CuBr estimated from the difference of the chemical potentials of copper ions allow the specific ionic conductivity to be calculated [6]. The time dependence $V_\mathrm{i}^\mathrm{i}(t)$ relates to the build-up and decay processes of the concentration polarization. Along the specimen length L the dropping of the concentration polarization after switching-off the ionic current, is expressed by the time dependence $V_\mathrm{i}^\mathrm{i}(t)$ [7]

$$V_\mathrm{i}^\mathrm{i}(t) = V_\mathrm{i}^\mathrm{i}(0) \exp\left(-\frac{\pi^2 \tilde{D} t}{L^2}\right), \tag{1}$$

where $V_\mathrm{i}^\mathrm{i}(0)$ is the potential difference at the moment of switching-off the current, $\tilde{D}$ is the chemical diffusion coefficient.

The degree of deviation from stoichiometry (δ) was controlled by the e.m.f. value E of the part of the cell (ii)

$$\mathrm{Pt_2} \mid \mathrm{Cu_{2-\delta}Te} \mid \mathrm{CuBr} \mid \mathrm{Cu} \mid \mathrm{Pt_4}\,,$$

using the previously obtained curves of the Coulometric titration $E = f(\delta)$, δ being changed by passing a definite quantity of charge through the cell (ii) during the experiment. Since CuBr is a purely ionic conductor [5], the quantity of charge (It) through the cell (ii) was used as a measure of the composition change. According to the Faraday law,

$$\Delta\delta = \frac{Lt}{n_\mathrm{x} F}, \tag{2}$$

where n_x is the number of non-metallic gram-atoms in the specimen and F the Faraday number.

To measure the ionic thermo-e.m.f. along the specimen in cell (i) a temperature gradient of 20 to 25 K/cm was established.

3. Results and Discussion

The X-ray spectra of the powder preparations are well indexed in the hexagonal lattice with the unit cell parameters $a = 1.2605$ nm and $c = 2.1750$ nm. Fig. 1 illustrates the temperature dependences of unit cell volume and lattice parameters.

Jumping changes of both the parameter a and the unit cell volume occur at 300 and 350 °C. Therefore, the phase transitions at these temperatures are first-order phase transformations.

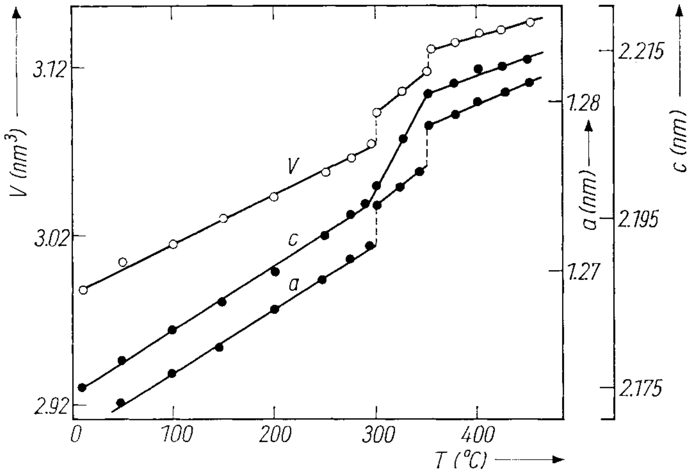

Fig. 1. Dependence of the lattice parameters a, c, and volume V on temperature for Cu_2Te

The dependences of the e.m.f. of the electrochemical cell (ii) on the degree of non-stoichiometry at various temperatures are shown in Fig. 2. The plateau of the dependence $E = f(\delta)$ corresponds to the two-phase region. It is clear from that figure that the extension of the homogeneity region of copper telluride increases with increasing temperature.

Fig. 3 and 5 show the dependences of the ionic conductivity and the chemical diffusion coefficient as a function of the degree of deviation from stoichiometry at various temperatures. Temperature dependences of the ionic conductivity and the thermo-e.m.f. are shown in Fig. 4 and 6.

3.1 Ionic conductivity

The ionic conductivity of $Cu_{2-\delta}Te$ and its functional dependence on the degree of non-stoichiometry are specified by two features. First, the high values of σ_i being a consequence of structural features of the system involved. Copper telluride belongs

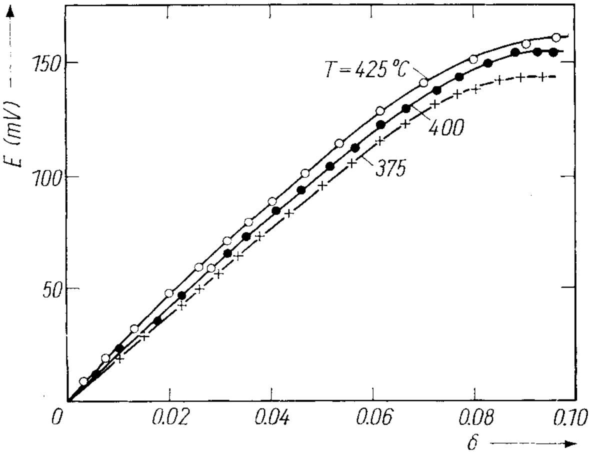

Fig. 2. Dependence of the cell-e.m.f. on the degree of non-stoichiometry at various temperatures

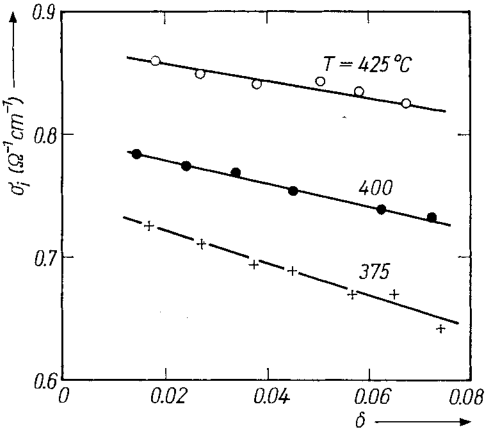

Fig. 3

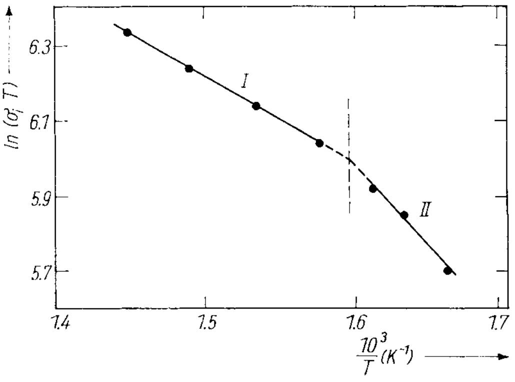

Fig. 4

Fig. 3. Dependence of the ionic conductivity on the degree of non-stoichiometry for $Cu_{2-\delta}Te$ at various temperatures

Fig. 4. Dependence of the ionic conductivity (in Ω^{-1} cm^{-1}) on reciprocal temperature for $Cu_{1.96}Te$

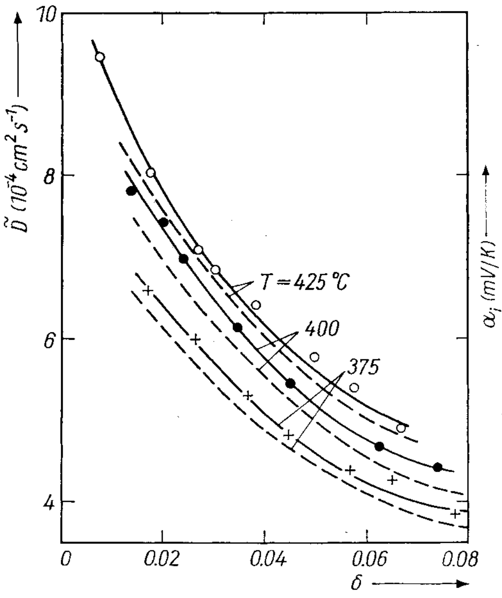

Fig. 5

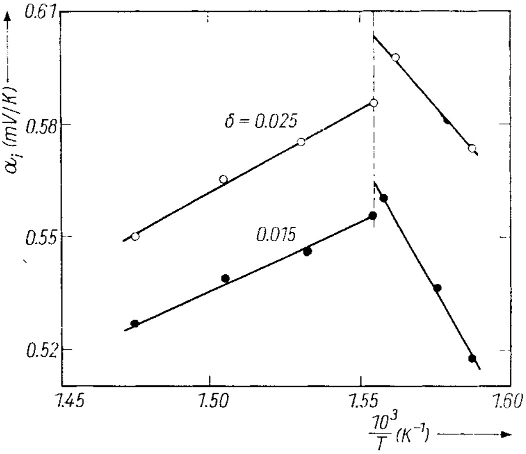

Fig. 6

Fig. 5. Dependence of the chemical diffusion coefficient on the degree of non-stoichiometry for $Cu_{2-\delta}Te$ at different temperatures. Symbols experimental, dashed curves calculation

Fig. 6. Dependence of ionic thermo-e.m.f. on temperature for $Cu_{2-\delta}Te$ at various δ

to the class of structurally disordered superionic conductors whose high conductivity is due to the fact that part of copper ions have weak bonding with the rigid frame. Second, the ionic conductivity decreases with deviation from the stoichiometric composition (Fig. 3), which may be explained only by a decrease of the concentration of mobile ionic carriers. The concentration of mobile ions is determined by structural features of the phase and is independent of temperature. Therefore, the temperature changes of the ionic conductivity is fully conditioned by changes of the copper ion mobility.

The ionic conductivity of superionic conductors may be expressed as [8]

$$\sigma_\mathrm{i} = \frac{q^2 v_0 f a^2}{kT} \varkappa N_\mathrm{i} \exp\left(-\frac{E_\mathrm{m}}{kT}\right), \tag{3}$$

where a is the jump length, f the correlation factor, v_0 the frequency of the ion oscillations in the vicinity of the equilibrium state, q the ion charge, N_i the number of ions per unit volume, $\varkappa$ the part of mobile ions, and E_m the activation energy for migration.

Fig. 4 shows the dependence $\ln(\sigma_\mathrm{i} T) = f(1/T)$ for the specimen of composition $Cu_{1.96}Te$. At the phase transition point at 350 °C a jumping change of the activation energy occurs. Above 350 °C the activation energy is equal to $E_\mathrm{a}^{(\mathrm{i})} = (0.20 \pm 0.02)$ eV and below it $E_\mathrm{a}^{(\mathrm{ii})} = (0.40 \pm 0.03)$ eV. It should be mentioned that copper telluride shows superionic properties both above and below the phase transition temperature, this transition being a superionic–superionic phase transition. Within the accuracy of experiment, the value of σ_i shows no jump near the phase transition point. For superionic conductors the following empirically established relation between the ionic conductivity value and the degree of disorder of the mobile ion sublattice n/n_i is true [8]:

$$\frac{\sigma_\mathrm{i}}{N_{\mathrm{Cu}^+}} = A \exp\left(B \frac{n}{n_{\mathrm{Cu}^+}}\right), \tag{4}$$

where N_{Cu^+} is the copper ion density per unit volume, n the number of possible positions of mobile ions in the unit cell, n_{Cu^+} the number of mobile ions in the elementary unit cell, A and B are constants. In comparison with other superionic conductors of the group of copper chalcogenides Cu_2S and Cu_2Se [9, 10], for $Cu_{2-\delta}Te$ (4) gives a comparatively low value of the ionic conductivity as a consequence of the smallness n/n_{Cu^+}. The hexagonal modification of Cu_2Te, specifically, yields the value 2 for n/n_{Cu^+}, whereas for copper sulfides and selenides with cubic symmetry the value is 6.

3.2 Chemical diffusion

When the ionic component of conductivity is measured, the use of electrodes blocking the electron current results in the development of concentration polarization of a gradient of the non-stoichiometry degree along the specimen. The rate of the concentration polarization build-up and decay is determined by the value of the chemical diffusion coefficient. In the general case, the chemical diffusion describes diffusion processes under the action of the chemical potential gradients of the particles. Copper telluride is a compound of variable composition with mainly electron conductivity and a high cation conductivity $\sigma_\mathrm{e} \gg \sigma_{\mathrm{Cu}^+}$, $\sigma_{\mathrm{Te}^{2-}} = 0$. For similar systems the relation between the coefficients of chemical diffusion and self-diffusion D_i may be written as [11]

$$\tilde{D} = \frac{N_\mathrm{i} D_\mathrm{i}}{kT} \frac{\mathrm{d}\mu_\mathrm{Cu}}{\mathrm{d}N_\mathrm{i}}, \tag{5}$$

where μ_Cu is the metal atom chemical potential in the phase concerned, N_i the ion concentration. The change of the metal atom chemical potential may be expressed by the e.m.f. of cell (ii) [2],

$$d\mu_{Cu} = e\, dE\,, \tag{6}$$

where e is the electron charge.

Expressing the copper ion concentration in $Cu_{2-\delta}Te$ as

$$N_i = \frac{N_A}{V_m}(2-\delta)\,, \tag{7}$$

where N_A is the Avogadro number and V_m the molar volume, (5) yields for the chemical diffusion coefficient

$$\tilde{D} = \frac{(2-\delta)\, D_i e}{kT}\, \frac{dE}{d\delta}\,. \tag{8}$$

The dashed lines in Fig. 5 shows dependences $\tilde{D}(\delta)$ estimated by (8) at various temperatures using experimental data on D_i and $E(\delta)$. The self-diffusion coefficient was calculated by the Nernst-Einstein relation from the ionic conductivity. There is a fairly satisfactory agreement between the experimental and calculated dependences of the chemical diffusion coefficients on the degree of non-stoichiometry. As compared to D_i, higher values of $\tilde{D}$ are due to the fact that copper ions are accelerated by the internal electric fields developing due to the difference between the mobilities of ions and electrons.

3.3 Ionic thermo-e.m.f.

The ionic thermo-e.m.f. is determined as the stationary electromotive force $\Delta\varphi_i$ measured between two ionic probes Cu/CuBr, if there is a temperature gradient along the specimen. According to [8], the coefficient of ionic thermo-e.m.f. is determined by

$$\alpha_i = \frac{\Delta\varphi_i}{\Delta T} = \frac{1}{e}\left(\frac{\partial\eta_i}{\partial T} + S^0_{Cu}\right), \tag{9}$$

where S^0_{Cu} is the copper atom entropy in metallic copper, η_i the copper ion electrochemical potential in $Cu_{2-\delta}Te$. The first term in (9) represents the homogeneous component of the ionic thermo-e.m.f. The second term is conditioned by the temperature dependence of the contact potential difference of electrode and phase and is a heterogeneous component of the ionic thermo-e.m.f. For the stationary value of α_i the phenomenological theory of the ionic thermo-e.m.f. of the superionic conductors yields

$$\alpha_i = -\frac{1}{e}\left(S_{Cu^+} - S^0_{Cu} + \frac{Q_{Cu^+}}{T}\right), \tag{10}$$

where S_{Cu^+} is the copper ion entropy in $Cu_{2-\delta}Te$, Q_{Cu^+} the copper ion transport heat in $Cu_{2-\delta}Te$.

The assumption of the temperature independence of the entropy difference is true for the majority of superionic conductors. Consequently, it is possible to determine the ion transport heat from the slope of the dependence $\alpha_i = f(1/T)$. The transport heat values thus determined are in satisfactory agreement with the values of the activation energy for ionic conduction of the silver superionic conductor group [8]. On the basis of such assumptions it was possible to determine the ion transport heat values for silver chalcogenides and solid solutions on their basis [12, 13] exhibiting mixed ion–electron conductivity, which are also in satisfactory agreement with the values of the activation energy for ionic conductivity. The dependence $\alpha_i(1/T)$ of $Cu_{2-\delta}Te$ for two values of δ is shown in Fig. 6.

At high temperatures a straight line in the coordinates $\alpha_i(1/T)$ is observed. At the phase transition point the ionic thermo-e.m.f. undergoes an anomaly. The anomalous dependence of α_i on temperature below the phase transition point seems to indicate that the specimen is not single-phase owing to a great temperature gradient along the specimen.

The calculation of the transport heat from the slope of the straight line $\alpha_i(1/T)$ for the high-temperature region yields 0.4 to 0.5 eV, this essentially exceeding the activation energy for ionic conduction. This is explained by the dependence of the entropy difference on temperature for copper telluride. Therefore, the research of the electrochemical cell (ii) at various temperatures (Fig. 2) has resulted in the determination of the value $(S_{Cu^+} - S^0_{Cu})$. Further, the transport heat was estimated from the known value α_i using (10). The copper ion transport heat thus estimated is $Q_{Cu^+} = (0.23 \mp 0.03)$ eV for $\delta = 0.015$ and $Q_{Cu^+} = (0.25 \mp 0.03)$ eV for $\delta = 0.025$. The values of transport heats in the high-temperature superionic phase correlate well with the values of the activation energy for ionic conduction.

4. Summary

The experimentally obtained results for copper telluride and their analysis show that $Cu_{2-\delta}Te$ undergoes a number of first-order phase transformations in the temperature range 300 to 450 °C. These transformations, however, do not result in a change of the lattice type or the degree of the cation sublattice disorder. In the range 300 to 450 °C copper telluride preserves the superionic properties and at the phase transition point the values of the activation energy for ionic conduction change spasmodically. The ionic conductivity in copper telluride is conditioned by the fact that part of cations have weak bonding with the rigid frame. The concentration of these cations is actually independent of temperature. Therefore, the activation energy for ionic conduction involves only the activation energy for mobility and the ion transport heat estimated from the ionic thermo-e.m.f. approximates the activation energy for ionic conduction. The deviation from stoichiometric composition results in a decrease of the concentration of mobile ions and, consequently, of the ionic conductivity at constant temperature. The process of establishing equilibrium in the specimen with the gradient of the degree of non-stoichiometry is determined from the chemical diffusion coefficient. A satisfactory agreement has been obtained for the experimental and phenomenologically estimated dependences of the chemical diffusion coefficients on the degree of non-stoichiometry.

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