Thermodynamic Properties of Ternary Phases in the Cu–Tl–Se System

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Abstract—The Cu–Tl–Se system has been studied at temperatures from 300 to 420 K using emf measurements with $Cu_4RbCl_3I_2$ as a Cu^+ ion conducting solid electrolyte. The emf data have been used to map out the subsolidus phase diagram of the Cu–Tl–Se system in the composition region Tl₂Se–CuTlSe–CuSe–Se. We have calculated the partial molar thermodynamic functions of the copper in the alloys and the standard thermodynamic functions of formation and standard entropies of the ternary compounds CuTlSe₂, CuTlSe, and Cu₂TlSe₂. The results confirm that the thermodynamic properties of copper-containing ternary systems can be studied using the approach in question even when they contain an element (thallium in this study) located to the left of copper in the electrochemical series.

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INTRODUCTION

Ternary copper and silver chalcogenides with heavy metals are potentially attractive electronic materials [1-3]. In particular, copper thallium tellurides and selenides are of interest for the development of advanced thermoelectric materials [4-6].

The development of physicochemical principles of the targeted synthesis of these compounds, new multicomponent phases, and related materials requires fundamental studies of phase equilibria and thermodynamic properties of phases in the systems involved [1, 2, 7]. In connection with this, we systematically studied the thermodynamic properties of ternary copper chalcogenides using solid-electrolyte emf measurements [8–11].

Solid-electrolyte emf measurements offer a number of advantages over classic liquid-electrolyte emf measurements. First, charge transport in solid electrolytes is due to one ionic species, in a fixed charge state, in contrast to that in liquid electrolytes. As a result, the charge of the potential-determining ion in equilibrium with the electrodes of a concentration cell is constant and stable. Moreover, permeable to only one ionic species, a solid electrolyte acts as a membrane separating two electrode compartments, thereby preventing many side processes associated with electrolyte–electrode and electrode–electrode interactions [7, 12].

Among Cu^+ ion conducting solid electrolytes, the highest ionic conductivity is offered by the compound $Cu_4RbCl_3I_2$ (melting point, 473 K), which was first identified in 1979 in a study of phase equilibria in the CuCl-CuI-RbCl system [12]. Even at room temperature, this compound has high (0.5 S/cm), almost purely ionic conductivity due to Cu⁺ (the electronic conductivity is as low as 5×10^{-16} S/cm) [12], which allows one to employ it in studies of copper-containing compounds, in particular, binary and ternary chalcogenides, as an electrolyte in concentration cells and to measure their emf at room temperature and above.

Classic liquid-electrolyte emf measurements are of limited utility in many copper-containing systems because it is difficult to ensure a constant charge (+1) of copper ions in liquid electrolytes and because there may be metals less noble than copper [7].

Phase equilibria in the Cu–Tl–Se system have not yet been studied in sufficient detail. Abishov et al. [13] reported a T-x phase diagram of the pseudobinary system Cu₂Se–Tl₂Se, which was found to contain the ternary compounds CuTlSe, Cu₇Tl₃Se₅, Cu₃TlSe₂, Cu₈Tl₂Se₅, and Cu₉TlSe₅. The CuTlSe–TlSe, CuTlSe–Tl, and CuTlSe–Se joins were also reported to be pseudobinary [14]. The first join has a simple eutectic phase diagram, the second has a monotectic phase diagram, and the third contains an incongruently melting ternary compound of composition CuTlSe₂.

Structural data are available for ten copper thallium selenides [2, 13–16]. In particular, CuTISe₂ and CuTISe crystallize in tetragonal symmetry with lattice parameters a = 5.83 Å, c = 11.62 Å (Z = 4, sp. gr. *I*42*d*) [15] and a = 4.08 Å, c = 8.16 Å (Z = 2, sp. gr. *P*4/*nmm*) [15], respectively [15] (according to Abishov et al. [16], a = 4.046 Å, c = 8.078 Å, Z = 2). Cu₃TISe₂ has a monoclinic structure with lattice parameters a = 15.213 Å, b = 4.0115 Å, and c = 8.3944 Å (sp. gr. C2/m) [15].

The purpose of this work was to study solid-state phase equilibria in the Cu–Tl–Se system in the composition region Tl_2Se –CuTlSe–CuSe–Se and the thermodynamic properties of the compounds CuTlSe₂, CuTlSe, and Cu₂TlSe₂.

EXPERIMENTAL

To study the $Tl_2Se-CuTlSe-CuSe-Se$ system, we first synthesized Tl_2Se , CuTlSe, and CuSe by melting stoichiometric high-purity elemental mixtures in evacuated (~ 10^{-2} Pa) silica ampules.

The congruently melting compounds Tl_2Se (663 K), TlSe (615 K) [17], and CuTlSe (693 K) [13] crystallize in homogeneous form from stoichiometric melts during slow cooling. To fully homogenize CuSe (incongruent melting at 655 K [17]), the melt was cooled from 1000 to 620 K, and the solidified material was held at this temperature for 500 h.

The synthesized compounds were identified by differential thermal analysis (DTA) and X-ray diffraction (XRD). Next, by melting appropriate mixtures of these compounds with elemental selenium, we prepared $Tl_2Se-CuTlSe-CuSe-Se$ alloys.

To drive the reactions to completion and equilibrate the materials, the alloys were heat-treated for a long time in three steps: 100 h at 600 K, 1000 h at 530 K, and 300 h at 450 K.

Next, the alloys were characterized by XRD (DRON-2 diffractometer, CuK_{α} radiation) and emf measurements using concentration cells of the type

 $(-)Cu(s) | Cu_4RbCl_3I_2(s) | (Cu-Tl-Se)(s)(+). (I)$

The compound $Cu_4RbCl_3I_2$, used as a solid electrolyte in cells of the type (I), was prepared by melting stoichiometric ratios of reagent-grade anhydrous CuCl, CuI, and RbCl in an evacuated (~10⁻² Pa) silica ampule at 900 K, followed by cooling to 450 K and homogenization by annealing at this temperature for 100 h [7, 9]. From the resultant cylindrical ingot, we cut ~4-mm-thick disks, which were used as solid electrolyte in cells of the type (I).

The right-hand electrode was fabricated by pressing powder of an annealed alloy into analogous disks.

The electrochemical cell design, similar to that described elsewhere [7], allowed us to simultaneously measure the emf of seven or eight samples. The cell was evacuated, filled with argon, and placed in a purpose-designed resistance-heated tube furnace, where it was thermostated at ~380 K for 40–50 h. The temperature was monitored by Chromel–Alumel thermocouples and mercury thermometers with an accuracy of ± 0.5 K.

The emf of the electrochemical cell was measured by a compensation technique with a V7-34A highresistance digital voltmeter at temperatures from 300 to 420 K. In this temperature range, the alloys under consideration are in the solid state and the compositions of equilibrium phases are essentially temperature-independent [13, 14].

The equilibrium emf was first measured after the electrochemical cell had been held at \sim 350 K for 40–60 h; subsequently, measurements were taken every 3–4 h after the temperature had stabilized. The concentration cells used were reversible, as evidenced by the good reproducibility of our results, the constant weights of the electrodes and electrolyte, and the constant color (slightly yellowish white) of the electrolyte.

RESULTS AND DISCUSSION

Using powder XRD data and emf measurement results for concentration cells of the type (I), we were able to assess solid-state phase equilibria in the Tl_2Se –CuTlSe–CuSe–Se system.

As seen in the figure, this system comprises seven three-phase regions. The variation of the emf with composition is fully consistent with the phase diagram: the emf is constant within each three-phase region, independent of the overall composition of the alloy, and changes sharply in going from one threephase region to another. At the same time, the emf changes only slightly in going from the $II + \alpha + TISe$ to the I + II + TISe region and from the I + II + III to the I + III + CuSe region (figure). The reason for this is that the emf measured in the former two regions was that of phase II, and the emf measured in the latter two regions was that of phase III. The composition dependence of the emf meets the known thermodynamic constraint [7] that the emf cannot decrease in going from Cu to $Tl_x Se_{1-x}$. This, and the linear variation of the emf with temperature, allowed us to use the emf measurement results for cells of the type (I) in thermodynamic calculations.

To evaluate the thermodynamic functions of the ternary compounds $CuTISe_2$, CuTISe, and Cu_2TISe_2 , we used the experimental data for the three-phase regions $CuTISe_2 + TISe + Se$, $CuTISe + CuTISe_2 + TISe$, and $Cu_2TISe_2 + CuTISe_2 + CuTISe$ (figure).

The emf data for these phase fields were represented by least squares linear equations [18] of the form [19]

$$E = a + bT \pm t \left[\frac{S_E^2}{n} + S_b^2 \left(T - \overline{T}\right)^2\right]^{1/2},$$

where *n* is the number of data points (*E* and *T*), S_E is the variance of an individual emf measurement, S_b is the variance of *b*, \overline{T} is the average absolute temperature, and *t* is Student's *t*. For a 95% confidence interval and a number of data points $n \ge 20$, we have $t \le 2$ [18].

From the equations thus obtained (Table 1), using well-known thermodynamic relations [7] we evaluated relative partial thermodynamic functions of the copper in the alloys at 298 K (Table 2).



Subsolidus phase equilibria in the $Tl_2Se-CuTISe-CuSe-Se$ system. The numbers in the three-phase regions specify the emf (mV) of concentration cells of the type (I) at 298 K.

According to the subsolidus phase diagram in the figure, the partial molar quantities in the phase fields indicated are the thermodynamic functions of the following potential-determining reactions (where all of the substances are crystalline):

$$Cu + TlSe + Se = CuTlSe_2,$$
(2)

$$Cu + TISe = CuTISe, (3)$$

$$Cu + CuTlSe_2 = Cu_2TlSe_2.$$
(4)

Note that the first reported Tl–Se phase diagram contained, in addition to Tl_2Se and TlSe, a compound of composition Tl_2Se_3 . Subsequently, however, the presence of this compound was not confirmed [17, 22]. For this reason, the potential-determining reaction (2) involves TlSe rather than Tl_2Se_3 .

Reaction schemes (2)-(4) can be used to evaluate the standard thermodynamic functions of formation and standard entropies of the ternary compounds. For example, according to reaction (2) we have for CuTlSe₂,

$$\Delta_{\rm f} Z^0 ({\rm CuTlSe}_2) = \Delta \overline{Z} ({\rm Cu}) + \Delta_{\rm f} Z^0 ({\rm TlSe}), \qquad (5)$$

$$S^{0}(CuTlSe_{2}) = \Delta \overline{S}(Cu) + S^{0}(Cu) + S^{0}(Se) + S^{0}(TlSe),$$
(6)

where $\Delta_{\rm f} Z^0 = \Delta_{\rm f} G^0$ or $\Delta_{\rm f} H^0$ of the corresponding compound, and $\Delta \overline{Z} = \Delta \overline{G}$ or $\Delta \overline{H}$.

In the calculations, we used the standard entropies of copper (33.15 \pm 0.08 J/(K mol) and selenium (42.13 \pm 2.09 J/(K mol)) [20, 21] and thermodynamic data for TISe (Table 3). The $\Delta_f G^0$ (298 K) and $-\Delta_f H^0$ (298 K) obtained by Vasil'ev et al. for thallium monoselenide from emf measurements [22] are recommended in modern handbooks as the most reliable values. The standard entropy of this compound calculated by us from the data from Vasil'ev et al. [22] also agrees well with values in handbooks [20, 21].

Also presented in Table 3 are thermodynamic data obtained for $CuTISe_2$ and CuTISe in Ref. [14] from emf measurements using concentration cells relative to a thallium electrode and previous data for copper

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Phase field	$E, \mathbf{mV} = a + bT \pm tS_E(T)$
$CuTlSe_2 + TlSe + Se$	$382.9 - 0.027T \pm 2 \left[\frac{0.35}{23} + 3.6 \times 10^{-5} \left(T - 360.4 \right)^2 \right]^{1/2}$
$CuTlSe + CuTlSe_2 + TlSe,$ $\alpha + CuTlSe + TlSe$	$211.4 + 0.138T \pm 2\left[\frac{0.21}{23} + 2.2 \times 10^{-5} \left(T - 358.7\right)^2\right]^{1/2}$
$Cu_2TlSe_2 + CuTlSe_2 + CuTlSe,$ $CuTlSe_2 + Cu_2TlSe_2 + CuSe$	$214.5 + 0.072T \pm 2\left[\frac{1.25}{23} + 7.4 \times 10^{-5} \left(T - 357.6\right)^2\right]^{1/2}$

Table 1. Temperature-dependent emf of concentration cells of the type (I) for some of the phase fields in the Cu–Tl–Se system

Table 2. Relative partial thermodynamic functions of the copper in Cu–Tl–Se alloys at 298 K

Phase field	$-\overline{\Delta G}(\mathrm{Cu})$	$-\overline{\Delta H}(\mathrm{Cu})$	$\overline{AS}(Cu)$ $L/(mol K)$
	kJ/mol		
$CuTlSe_2 + TlSe + Se$	36.169 ± 0.076	36.94 ± 0.42	-2.61 ± 1.16
$CuTlSe + CuTlSe_2 + TlSe, \alpha + CuTlSe + TlSe$	24.365 ± 0.058	20.40 ± 0.32	13.32 ± 0.91
$Cu_2TlSe_2 + CuTlSe_2 + CuTlSe, CuTlSe_2 + Cu_2TlSe_2 + CuSe$	22.767 ± 0.108	20.70 ± 0.59	6.95 ± 1.66

Table 3. Standard thermodynamic functions of formation and standard entropies of phases in the Cu-Tl-Te system

Compound	$-\Delta_{\rm f}G^0(298~{ m K})$	$-\Delta_{\rm f} H^0$ (298 K)	$S^{0}(298 \text{ K}) = 1/(\text{mol K})$	
	kJ/mol		5 (298 K), J/(1101 K)	
TlSe [20-22]	60.12 ± 0.10	60.97 ± 0.53	103.4 ± 1.8	
CuTlSe ₂	96.29 ± 0.16 96.5 ± 0.6 [2, 14]	97.91 ± 0.95 97.2 ± 1.3 [2,14]	176.1 ± 5.1	
CuTlSe	84.49 ± 0.16 84.2 ± 1.3 [2, 14]	81.37 ± 0.85 80.5 ± 3.9 [2, 14]	149.9 ± 2.8	
Cu ₂ TlSe ₂	119.06 ± 0.27	118.61 ± 1.54	216.2 ± 6.8	

selenides. As seen, the thermodynamic functions of formation obtained for these compounds by emf measurements using different electrodes and different potential-determining reactions are in reasonable agreement.

CONCLUSIONS

Using emf measurements on concentration cells relative to a copper electrode with $Cu_4RbCl_3I_2$ solid electrolyte, we obtained a self-consistent set of thermodynamic functions of formation and standard entropies for three ternary compounds in the Cu–Tl–Se system.

The data lend support to the conclusion drawn earlier [10] that the superionic conductor $Cu_4RbCl_3I_2$ can be successfully used as a solid electrolyte in thermodynamic studies of copper-containing systems even

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when they contain an element (thallium in this study) located to the left of copper in the electrochemical series. The reason for this is that, in contrast to liquid electrolytes, solid electrolytes prevent side processes (electrolyte–electrode and electrode–electrode interactions) and thus allow one to obtain reproducible data with concentration cells that are irreversible in the classic sense.

This advantage of cation-conducting solid electrolytes considerably extends the range of systems that can be characterized by emf measurements.

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