Calculation of thermodynamic functions of saturated solid solution of AgIn$_2$Te$_3$I compound in the Ag–In–Te–I system

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Abstract. Triangulation of Ag–In–Te–I system in the vicinity of AgIn$_2$Te$_3$I compound was investigated by X-ray diffraction and differential thermal analysis methods. The spatial position of the phase region AgIn$_2$Te$_3$I–InTe–Ag$_2$Te–AgI regarding the figurative point of silver was used in order to write the equation of virtual potential-forming reaction. Potential-forming reaction was performed in electrochemical cell (ECC) of the type (–) C | Ag | Ag$_3$GeS$_3$I(Br) glass | *D* | C (+) where C are inert (graphite) electrodes; Ag and *D* are the electrodes of the ECC; *D* represents the alloy of four-phase region; Ag$_3$GeS$_3$I glass is a membrane with purely ionic Ag$^+$ conductivity). Linear dependence of the EMF of cell on temperature in the range of 440–480 K was used to calculate the standard thermodynamic functions of saturated solid solution of AgIn$_2$Te$_3$I compound in Ag–In–Te–I system.

1 Introduction

In recent years, there has been an increasing interest in solid ionic conductors in view of the need to develop novel devices such as micro- and nano supercapacitors, ion selective membranes, batteries, fuel cells, sensors, electrochromic displays, etc [1, 2]. The AgIn$_2$X$_3$Y compounds (X – S, Se, Te; Y – Cl, Br, I) belong to the group of silver-containing chalcogenide crystalline Ag$_3$SI(Br) and glassy Ag$_3$GeS$_3$I(Br) superionic phases in which chalcogenide anions, along with silver cations, possess the properties of non-stationary quasi-liquids [3].

This paper presents the results of the experimental determination of the boundaries of phase regions including the AgIn$_2$Te$_3$I compound, and calculation of thermodynamic functions of saturated solid solution of the four-element compound.

2 Experimental

The InTe, In$_2$Te$_3$, Ag$_2$Te compounds were prepared by cooling of the melts of the mix of the elements of semiconductor purity. The Ag$_3$GeS$_3$I glass was obtained by quenching the melt of elements and AgI from 1200 K into ice water. Crystals of indium and silver tellurides (particle size ≤5 µm) together with powdered AgI were used for making the positive electrodes of electrochemical cell (ECC) and for alloys for differential thermal analysis (DTA) and X-ray diffraction (XRD). Well-mixed blends of calculated quantities of the compounds were placed into quartz ampoules and evacuated to the residual pressure ~ 1 Pa. Solid-phase synthesis was performed at 820 K for 20 days. The phase composition of the alloys was determined by DTA and XRD. XRD patterns were collected on a STOE STADI P diffractometer [4] equipped with a linear position–sensitive detector PSD, in a modified Guinier geometry (transmission mode, CuKα$_1$ radiation, a bent Ge (111) monochromator, 2θ/ω scan mode). XRD arrays were processed using STOE WinX^{POW} (version 2.21) and PowderCell (version 2.3) software suits.

Potential-forming process was performed in electrochemical cell of the type (–) C | Ag | Ag$_3$GeS$_3$I glass | *D* | C (+) where C are the inert graphite electrodes; Ag and *D* are the electrodes of ECC; *D* represents the alloy of four-phase region; and Ag$_3$GeS$_3$I glass is a membrane with purely ionic Ag$^+$ conductivity.

Powdered cell components were pressed ($p \sim 10^8$ Pa) into through holes with the diameter of 2 mm arranged in the PTFE matrix up to the density $\rho = (0.93 \pm 0.02)\rho_0$, where ρ_0 is the experimentally determined density of cast alloys. To eliminate the defects of plastic deformation under extrusion of alloys, we performed five-fold thermal cycling of ECC in the range of 400–480 K with heating and cooling rates of 2 K min^{-1}. The ECC was heated in a resistance furnace filled with a mixture of H$_2$ and Ar in a molar ratio of 1 : 9, $p = 1.2 \times 10^5$ Pa. The flow of gas at the rate of 2×10^{-3} m^3 h^{-1} had a direction from the positive to the negative electrode of the ECC. The temperature was maintained with an accuracy of ±0.5 K. The EMF values of the cells were measured using the voltmeter of a U7–9 electrometric amplifier with an input resistance of $>10^{12}$ Ω.

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3 Results and discussion

According to Fig. 1, virtual chemical reaction in the ECC involving four-element phase is described by the equation
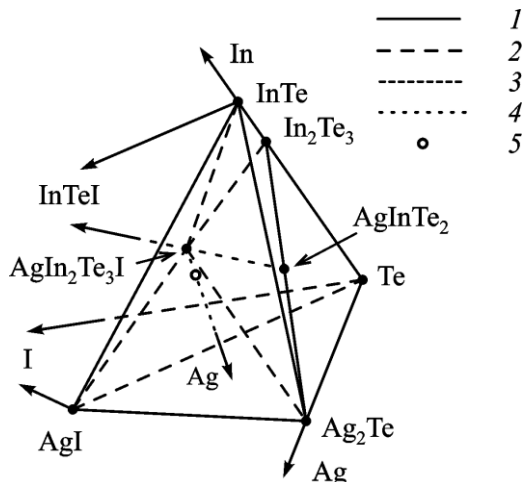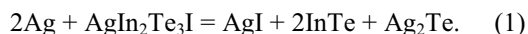
$$2Ag + AgIn_2Te_3I = AgI + 2InTe + Ag_2Te. \quad (1)$$

Fig. 1. Triangulation of the Ag–In–Te–I system in the vicinity of AgIn$_2$Te$_3$I compounds: *1, 2* are the lines of two-phase equilibria; *3, 4* are the sections Ag–AgIn$_2$Te$_3$I and AgInTe$_2$–InTeI; *5* is the figurative point of the alloy of the positive electrode of ECC.

The equation is written in the approximation of little difference between the position of figurative point of the compound and of its saturated solid solutions in Gibbs tetrahedron. Based on Eq. (1) the positive electrode of ECC was formed from the mixture of powdered silver and compounds AgI, In$_2$Te$_3$, in the molar ratio Ag : AgI : In$_2$Te$_3$ = 1 : 1 : 1. The linear dependence EMF (*E*) on temperature (*T*) for ECC with positive electrodes *D* in the range 440–480 K is approximated by the equation

$$E / mV = (164.67971 \pm 0.86451) + $$
$$+ (0.16850 \pm 0.00186)T / K. \quad (2)$$

The deviation from the linearity above 480 K is likely due to the changes in the regions of the existence of the phases.

From the measured *E*(*T*) relation, Gibbs energy was calculated using the basic thermodynamic equation

$$-\Delta_r G_T = n\, F\, E(T), \quad (3)$$

where $n_e = 2$ is a number of electrons taking part in the reaction (1); F = 96485.3 C mol^{-1} is Faraday's number.

According to (1)

$$\Delta_r G_{T,(1)} = 0.5\Delta_f G_{T,\beta-Ag_2Te} + \Delta_f G_{T,InTe} +, \quad (4)$$
$$+0.5\Delta_f G_{T,\beta-AgI} - 0.5\Delta_f G_{T,\beta-AgIn_2Te_3I}$$

where $\Delta_f G_T$ are the Gibbs energies of the formation of the appropriate phase from the elements at temperature *T*.

From Eq. (2) the Gibbs energy of the formation of AgIn$_2$Te$_3$I is then:

$$\Delta_f G_{T,\,AgIn_2Te_3I} = \Delta_f G_{T,\beta-Ag_2Te} + 2\Delta_f G_{T,InTe} +, \quad (5)$$
$$+\Delta_f G_{T,\beta-AgI} - 2\Delta_r G_{T,(1)}$$

Considering that $\Delta_f G_{T,\,Ag2Te}$=(−26.0129±1.858)− (42.8±9)×10^{-3}T [5], $\Delta_f G_{T,\,InTe}$= −71.965+1.634×10^{-3}T, $\Delta_f G_{T,\,\beta-AgI}$ = −63.214 − 14.19×10^{-3}T [6], and using Eqs. (2) and (3) we obtained

$$\Delta_f G_{T,\,AgIn2Te3I}/(kJ\ mol^{-1}) = (-201.4 \pm 1.9) - $$
$$- (21.2 \pm 9.5) \times 10^{-3}T/K. \quad (6)$$

Eq. (6) expresses the temperature dependence of the Gibbs energy of the formation of the saturated solid solution of four-element compound in phase region Ag$_2$Te–InTe–AgIn$_2$Te$_3$I–AgI of the Ag–In–Te–I system. The values of the thermodynamic functions of four-element phase were calculated according in the approximation ΔC_p=const.

4 Conclusions

1. The analytical equation of the temperature dependence of Gibbs energy of the formation from elements of the saturated solid solution of the compound AgIn$_2$Te$_3$I in the region AgIn$_2$Te$_3$I–InTe–Ag$_2$Te–AgI (I) was obtained.

2. The values of standard integral thermodynamic functions of four-element phase in phase regions (I) were calculated.

3. The symmetry of the lattice of AgIn$_2$Te$_3$I compound with the formation of the solid solution is decreased.

References

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