THERMODYNAMIC PROPERTIES OF $TlSnSe_2$ AND Tl_2SnSe_3 COMPOUNDS

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The temperature and concentration dependences of electromotive force (E.M.F.) for alloys of SnSe – TlSe system have been investigated in temperature interval 300-420K. The values of Gibbs energy, enthalpy and entropy of compound formation of $TlSnSe_2$ and Tl_2SnSe_3 compositions have been calculated from temperature dependence equation of E.M.F. The absolute entropies and enthalpies of phase atomization characterizing the chemical bond strength have been also obtained.

The state diagram of TlSe-SnSe system is characterized by compounds of $TlSnSe_2$ and Tl_2SnSe_3 compositions (fig.1) which are semiconductors [1].

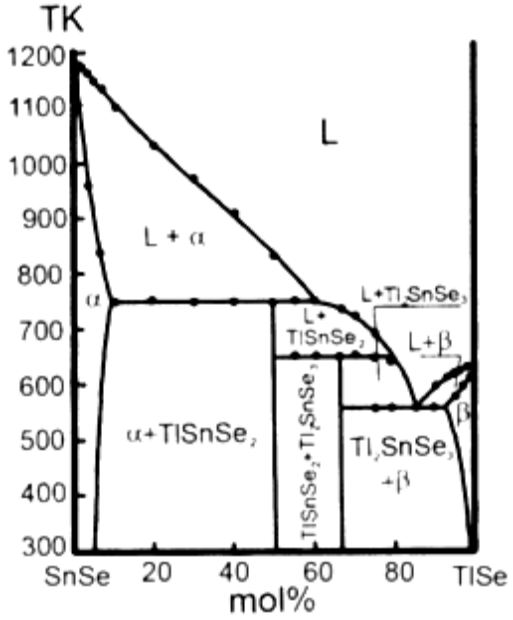

Fig.1. State diagram of SnSe – TlSe system

The method of thermoelectromotive forces (E.M.F.) the p[principal foundations of which is described in work [2] has been chosen by us for investigation of above mentioned thermodynamic properties. E.F.M of electrochemical chains which are concentration ones with respect to electrodes at 300÷420K are measured

$$\{-\}\,Tl|TlCl,KCl,\ glycerol|[(TlSe)_x(SnSe)_{1-x}]\ \{+\}$$

where x is mole fraction of TlSe in the alloy. The electrolyte is the dehydrated sweet solution of potassium chloride (4weight%) and thallium chloride (0,1weight%).

The investigations are carried out in the correspondence with state diagram within the separate phase fields. The samples for experiment are prepared by the allowing of thallium and tin selenides previously synthesized from elementary components (thallium, selenium, tin) in the quartz ampoules evacuated up to residual pressure 10^{-4} millimeter of mercury during 8 hours at temperature 900÷1000K. After synthesis the samples are treated by annealing during 100 hours at 600K. The electrodes are prepared by pressing of powders of investigated samples.

The measured dependence E.M.F on the composition confirms the state diagram constructed earlier by DTA and DTPh methods and microhardness measurements [1]. The E.M.F. data collection for each heterogeneous region is processed simultaneously and then the equations of E.M.F. dependence on temperature are worked out (fig.2 and 3).

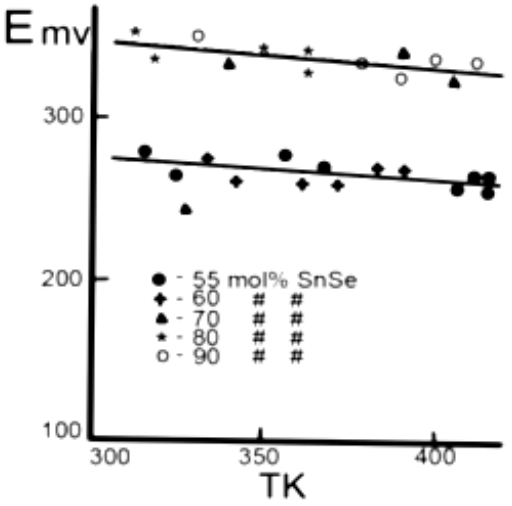

Fig.2. The dependence of E.M.F. on temperature of SnSe – TlSe system alloys.

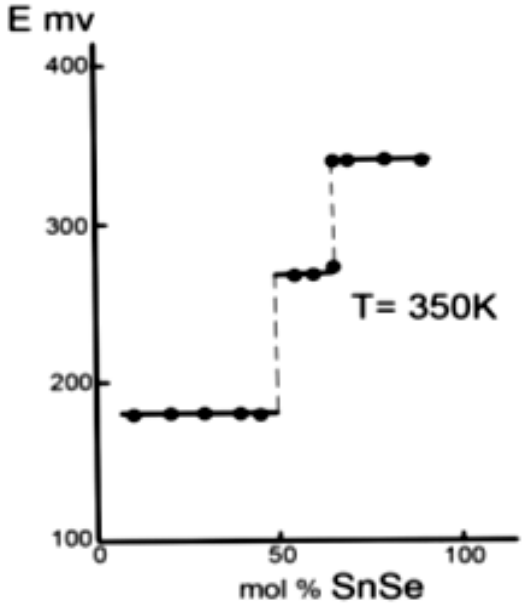

Fig.3. The concentration dependence of E.F.M. on temperature of SnSe – TlSe system alloys.

The method of least quadrates [3] is used at experiment data processing.

The experimental results of temperature dependence of E.M.F. for each heterogeneous region of system state diagram are given in the table 1.

Table 1.

Experimental dependence $E = f(T)$

Phase region	Temperature interval K	Potential generating reaction	$E = f(T)$, V
$SnSe - TlSnSe_2$	300 – 420	$TlSe + SnSe = TlSnSe_2$	$(0{,}3741\text{-}0{,}096\cdot T\cdot 10^{-3}) \pm 4\cdot 10^{-3}$
$TlSnSe_2 - TlSnSe_3$	300 – 420	$TlSe + TlSnSe_2 = Tl_2SnSe_3$	$(0{,}3067\text{-}0{,}1023\cdot T\cdot 10^{-3}) \pm 4\cdot 10^{-3}$

The sequential combining of $E=f(T)$ equations and application of known relations of thermodynamics:

$$\Delta G^0 = -Z\cdot F\cdot E, \quad \Delta S^0 = zF\cdot(dE/dT)p,$$

$$\Delta H^0 = zF\cdot[(dE/dT)p] - E$$

allow us to calculate the standard thermodynamic forming functions of triple compound $TlSnSe_2$ and Tl_2SnSe_3 from elements in hard state. The necessary reference data are taken from [4-7]. The values of Gibbs energy, enthalpy and entropy of formation and also values of atom formation heat of $TlSnSe_2$ and Tl_2SnSe_3 triple compounds are presented in table2.

Table 2

Thermodynamic formation functions of $TlSnSe_2$ and Tl_2SnSe_3 compounds at 298K

	$-\Delta G^0$	$-\Delta H^0$	ΔH^{am}	$-\Delta S^0$	S^0
Compound	kJ/mol			J/mol· K	
$TlSnSe_2$	124,36±1,42	127,91±14,11	982,6	9,37±2,62	183,66±2,62
Tl_2SnSe_3	151,07±1,70	157,08±17,20	1379,3	19,23±4,18	280,39±4,18

CONCLUSION

The thermodynamic investigations of SnSe – TlSe system is carried out by E.F.M. measuring method of concentration electrochemical chains and its state diagram is proved. The data on Gibbs energy, enthalpy and entropy of formation, absolute atom formation entropy and enthalpy characterizing the of chemical bond strength for $TlSnSe_2$ and Tl_2SnSe_3 triple compounds are obtained.

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$TlSnSe_2$ VƏ Tl_2SnSe_3 BİRLƏŞMƏLƏRİN TERMODİNAMİK XƏSSƏLƏRİ

İlk dəfə olaraq SnSe – TlSe sistemində Elektrik Hərəkət Qüvvəsinin temperaturdan (300-420K) və qatılıqdan asılılığı öyrənilmişdir. $TlSnSe_2$ və Tl_2SnSe_3 birləşmələrin əmələ gəlmə Qibbs enerjisı, entalpiyası, atomizasiya enerjisı hesablanmışdır.

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ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА СОЕДИНЕНИЙ $TlSnSe_2$ И Tl_2SnSe_3

В интервале температур 300-420К получены данные по температурной и концентрационной зависимостей Э.Д.С. сплавов системы SnSe – TlSe. Из уравнения температурной зависимости Э.Д.С. рассчитаны значения энергии Гиббса, энтальпии и энтропии образования соединений составов $TlSnSe_2$ и Tl_2SnSe_3. Определены также абсолютные энтропии и энтальпии атомизации фаз, характеризующие прочность химической связи.

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