Thermodynamic Properties of the SnSb$_2$Te$_4$ Compound

F. N. Guseinov[a], A. E. Seidzade[a], Yu. A. Yusibov[b], and M. B. Babanly[a]*

*[a]Nagiyev Institute of Catalysis and Inorganic Chemistry, Academy of Sciences of Azerbaijan,
Javid ave.113, Baku, AZ1143 Azerbaijan*
[b]Ganja State University, H. Aliyev ave. 187, Ganja, AZ2000 Azerbaijan
*e-mail: Babanly_mb@rambler.ru

Abstract—The SnTe–Sb$_2$Te$_3$–Te system has been studied in the temperature range 300–430 K using emf measurements on reversible concentration cells of the type (−)SnTe(s) | liquid electrolyte, Sn^{2+} | (Sn–Sb–Te)(s)(+). The system has been shown to consist of two three-phase regions, separated by the SnSb$_2$Te$_4$–Te tie line. The best fit equation for the temperature-dependent emf data has been used to evaluate the partial thermodynamic functions of the SnTe and Sn in the alloys. Using these data, subsolidus phase diagram data for the SnTe–Sb$_2$Te$_3$–Te system, and relevant thermodynamic functions for SnTe and Sb$_2$Te$_3$, we calculated the standard Gibbs energy of formation, standard enthalpy of formation, and standard entropy of the SnSb$_2$Te$_4$ compound.

Keywords: tin antimony telluride, SnSb$_2$Te$_4$, emf measurements, thermodynamic properties

INTRODUCTION

The tetradymite-like ternary compounds with the general formulas $A^{IV}B_2^VTe_4$, $A^{IV}B_4^VTe_7$, $A^{IV}B_6^VTe_{10}$, and others in the $A^{IV}–B^V–Te$ (A^{IV} = Ge, Sn, Pb; B^V = Sb, Bi) systems are potentially attractive thermoelectric materials having low thermal conductivity [1–4]. These compounds have complex, multilayer structures, and their lattice thermal conductivity is lower than that of the constituent binary compounds $A^{IV}Te$ and $B_2^VTe_3$, which is important for thermoelectric applications. According to recent work [5–8], the ternary compounds in question are three-dimensional topological insulators and can be used in spintronics and quantum computation.

The ability to optimize synthesis and crystal growth conditions for multicomponent phases depends crucially on knowledge of their thermodynamic functions. Given this, we undertook a thermodynamic study of the above ternary compounds using emf measurements. Previously, we reported results of detailed studies of solid-state phase equilibria in the SnTe–Bi$_2$Te$_3$–Te and PbTe–Bi$_2$Te$_3$–Te systems and the standard thermodynamic functions of the compounds and solid solutions existing in these systems [9, 10].

As a continuation of our previous work on such systems, in this article we present results of a thermodynamic study of the SnTe–Sb$_2$Te$_3$–Te system with the use of emf measurements.

Phase equilibria in the ternary system Sn–Sb–Te have been addressed in a number of studies. The results of early work were summarized by Shelimova et al. [4]. Elagina and Abrikosov [11] presented a phase diagram of the pseudobinary system SnTe–Sb$_2$Te$_3$, and Stegherr [12] reported a total $T–x–y$ phase diagram of the Sn–Sb–Te system and a number of its vertical sections. As shown earlier [4, 11, 12], the pseudobinary system SnTe–Sb$_2$Te$_3$ contains a compound with the composition SnSb$_2$Te$_4$, which melts incongruently at 879 [11] or 876 K [12]. This compound crystallizes in a hexagonal tetradymite-like structure (sp. gr. $\bar{R}3m$) with unit-cell parameters $a = 0.4294$ nm and $c = 4.1548$ nm ($Z = 3$) [13].

EXPERIMENTAL

For our experiments, we synthesized the compounds SnTe, Sb$_2$Te$_3$, and SnSb$_2$Te$_4$. The first two compounds melt congruently at 1079 and 891 K [14], respectively, and the third decomposes peritectically at 876 K. Mixtures of high-purity elemental tin, antimony, and tellurium were reacted at a temperature slightly above the melting point of the corresponding compound, in a silica ampule pumped down to ~10^{-2} Pa, which was then furnace-cooled. To ensure complete homogenization, the synthesized SnSb$_2$Te$_4$ was cooled to a temperature of 800 K and held there for 200 h.

Alloys of the SnTe–Sb$_2$Te$_3$–Te system were prepared from presynthesized and identified compounds
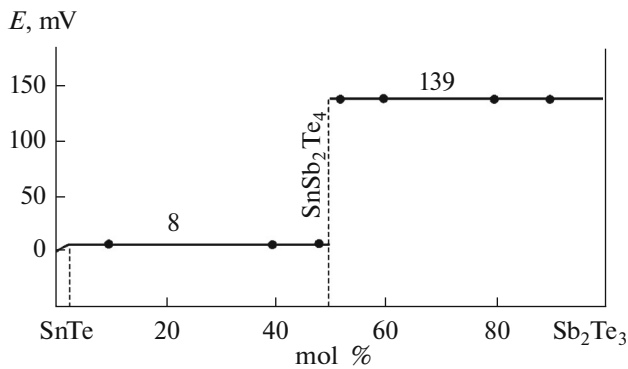
Composition dependence of the 300 K emf of concentration cells of the type (1) for the SnTe–Sb$_2$Te$_3$ system.

and elemental tellurium, which were melted together under vacuum. The resultant alloys were annealed at 600 K for 500 h.

The thermodynamic properties of the alloys were studied using concentration cells of the type

$$(-)SnTe(s) \mid \text{liquid electrolyte,}$$
$$Sn^{2+} \mid (SnTe-Sb_2Te_3-Te)(+), \quad (1)$$
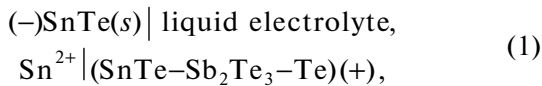
because concentration cells turned out to be irreversible to tin electrodes, as in a previous study [9].

The electrodes were fabricated by pressing powdered SnTe (left-hand electrode) and annealed alloys of the system under investigation (right-hand electrodes) into pellets 0.8–1 cm in diameter and 0.4–0.6 cm in thickness.

The electrolyte used was a glycerol solution of KCl with SnCl$_2$ additions. Given that the electrolyte must be free of moisture and oxygen, the glycerol (analytical grade) was thoroughly dried and degassed at a temperature of 400 K under dynamic vacuum, and reagent-grade anhydrous KCl and SnCl$_2$ were used.

The procedures utilized to set up electrochemical cells and measure their emf were described in detail elsewhere [15, 16]. The emf was measured from 300 to 430 K in an inert atmosphere by a compensation technique using a V7-34A digital voltmeter.

RESULTS AND DISCUSSION

The experimental emf data for the cells of the form (1) were well consistent with the phase diagram of the Sn–Sb–Te system [4]. In the composition region SnTe–Sb$_2$Te$_3$–Te, we obtained two series of emf values, which corresponded to the three-phase regions SnTe–SnSb$_2$Te$_4$–Te and SnSb$_2$Te$_4$–Sb$_2$Te$_3$–Te of the phase diagram.

The figure shows the composition dependence of the 300 K emf along the SnTe–Sb$_2$Te$_3$ join. It is seen that the emf isotherm comprises two horizontal portions with emf values of 8 and 139 mV, with a sharp step

at the stoichiometric composition of the SnSb$_2$Te$_4$ compound. This suggests that SnSb$_2$Te$_4$ has no considerable homogeneity range in the temperature range of our emf measurements. It is worth noting that the nonzero emf of the alloys containing <50 mol % SnTe can be interpreted as indirect evidence that the system has a narrow range of SnTe-based solid solutions.

In our thermodynamic calculations, the experimental emf data for the SnSb$_2$Te$_4$–Sb$_2$Te$_3$–Te three-phase region were analyzed using least squares fitting under the assumption that the emf was a linear function of temperature [17], and the results were represented by equations of the form

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

recommended by Morachevskii et al. [15] and Babanly and Yusibov [16]. Here, n is the number of data points (E versus T), S_E is the variance of an individual emf measurement, S_b is the variance of the coefficient 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 $n \geq 20$, we have $t \leq 2$.

Using the equation thus obtained,

$$E,\text{ mV} = 124.4 + 0.048T$$
$$\pm 2[(0.25/23) + 6.1 \times 10^{-6}\,(T - 364.7)^2]^{1/2}$$

and well-known thermodynamic relations [15, 16], we evaluated partial molar thermodynamic functions of the SnTe in the alloys at 298 K:

$$\overline{\Delta G}_{\text{SnTe}} = -26.00 \pm 0.08 \text{ kJ/mol,}$$

$$\overline{\Delta H}_{\text{SnTe}} = -23.23 \pm 0.35 \text{ kJ/mol,}$$

$$\overline{\Delta S}_{\text{SnTe}} = 9.26 \pm 0.96 \text{ J/(K mol).}$$

These functions are the differences between the partial molar functions of the tin in SnTe and SnSb$_2$Te$_4$:

$$\overline{\Delta Z}_{\text{SnTe}} = \overline{\Delta Z}_{\text{Sn}} - \overline{\Delta Z}'_{\text{Sn}}, \quad (3)$$

where $\overline{\Delta Z}'_{\text{Sn}}$ and $\overline{\Delta Z}_{\text{Sn}}$ are the partial thermodynamic functions of the tin in SnTe and SnSb$_2$Te$_4$, respectively.

On the other hand, since SnTe is the only compound in the Sn–Te system [14], the following relation is valid for it [16]:

$$\overline{\Delta Z}'_{\text{Sn}} = \Delta_f Z^0(\text{SnTe}). \quad (4)$$

Combining relations (3) and (4), we obtain

$$\overline{\Delta Z}'_{\text{Sn}} = \overline{\Delta Z}_{\text{SnTe}} + \Delta_f Z^0\,(\text{SnTe}). \quad (5)$$

According to Morachevskii et al. [15], Babanly and Yusibov [16], and the phase diagram of the Sn–Sb–Te system [4], the functions $\overline{\Delta Z}_{\text{Sn}}$ in the SnSb$_2$Te$_4$–Sb$_2$Te$_3$–Te three-phase region are the thermodynamic

Standard integral thermodynamic functions of the compounds SnTe, Sb_2Te_3, and $SnSb_2Te_4$

Compound	$-\Delta_f G^0$ (298 K)	$-\Delta_f H^0$ (298 K)	S^0(298 K), J/(K mol)
	kJ/mol		
SnTe	60.8 ± 1.0	60.7 ± 0.8 [18−21]	101.3 ± 4.2 [20, 22]
Sb_2Te_3	58.6 ± 1.0	56.5 ± 0.8 [18−21]	246.4 ± 2.1 [18, 20, 22]
$SnSb_2Te_4$	145.4 ± 1.9	140.4 ± 1.6	357.2 ± 7.7

functions of the following potential-determining reaction: $Sn + Sb_2Te_3 + Te = SnSb_2Te_4$.

For the standard thermodynamic functions of formation of the $SnSb_2Te_4$ compound, we then obtain the relation

$$\Delta_f Z^0(SnSb_2Te_4) = \overline{\Delta Z}_{Sn} + \Delta_f Z^0(Sb_2Te_3) \quad (6)$$

(where $Z = G$ or H), and its standard entropy meets the relation

$$S^0(SnSb_2Te_4) = \overline{\Delta S}_{Sn} + S^0(Sn) + S^0(Sb_2Te_3) + S^0(Te). \quad (7)$$

In calculations using relations (5)−(7), we employed published data on the relevant thermodynamic characteristics of SnTe and Sb_2Te_3 (table) and the standard entropies of white tin (51.55 ± 0.21 J/(K mol) and tellurium (49.50 ± 0.21 J/(K mol)) presented in Ref. [19]. The standard integral thermodynamic functions of SnTe and Sb_2Te_3 used in our calculations are self-consistent and quite reliable. The standard heats of formation and standard entropies recommended in various handbooks and review articles [18−22] for these compounds are essentially identical, and their standard Gibbs energies of formation calculated by us from their enthalpy and entropy of formation agree very well with data inferred from emf measurements [20−22].

As a result of the calculations by Eq. (5), we obtained the following partial molar functions of the tin in $SnSb_2Te_4$:

$$\overline{\Delta G}_{Sn} = -86.8 \pm 0.9 \text{ kJ/mol},$$

$$\overline{\Delta H}_{Sn} = -83.9 \pm 1.2 \text{ kJ/mol},$$

$$\overline{\Delta S}_{Sn} = 9.7 \pm 5.3 \text{ J/(K mol)}.$$

The standard integral thermodynamic functions of the $SnSb_2Te_4$ compound calculated using relations (6) and (7), the above data, and the relevant thermodynamic functions of the constituent binary compounds are presented in the table. Uncertainties were evaluated by the error propagation method.

CONCLUSIONS

Using emf measurements, we obtained self-consistent data on the standard integral thermodynamic functions of the $SnSb_2Te_4$ compound, which is of great practical interest as a thermoelectric material and three-dimensional topological insulator.

REFERENCES

1. Shevel'kov, A.V., Chemical aspects of thermoelectric materials engineering, *Usp. Khim.,* 2008, vol. 77, no. 1, pp. 3−21.

2. Kanatzidis, M.G., The role of solid state chemistry in the discovery of new thermoelectric materials, *Semicond. Semimet.,* 2001, vol. 69, pp. 51−98.

3. Shelimova, L.I., Karpinskii, O.G., Zemskov, V.S., et al., Promising thermoelectric materials based on tetradymite-like layered chalcogenides, *Perspekt. Mater.,* 2000, no. 5, pp. 23−32.

4. Shelimova, L.E., Tomashik, V.N., and Grytsiv, V.I., *Diagrammy sostoyaniya v poluprovodnikovom materialovedenii. Spravochnik* (Phase Diagrams in Semiconductor Materials Research: A Handbook), Moscow: Nauka, 1991.

5. Niesner, D., Otto, S., Hermann, V., Fauster, Th., et al., Bulk and surface electron dynamics in a *p*-type topological insulator $SnSb_2Te_4$, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2014, vol. 89, paper 081 404.

6. Okamoto, K., Kuroda, K., Miyahara, H., and Miyamoto, K., Observation of a highly spin polarized topological surface state in $GeBi_2Te_4$, *Phys. Rev. B: Condens. Matter Mater. Phys.,* 2012, vol. 86, pp. 195304−195308.

7. Viti, L., Coquillat, D., Politano, A., Kokh, K.A., et al., Plasma-wave terahertz detection mediated by topological insulators surface states, *Nano Lett.,* 2016, vol. 16, pp. 80−87.

8. Papagno, M., Eremeev, S., Fujii, J., Aliev, Z.S., et al., Multiple coexisting Dirac surface states in three-dimensional topological insulator $PbBi_6Te_{10}$, *ACS Nano,* 2016, vol. 10, pp. 3518−3524.

9. Babanly, M.B., Guseinov, F.N., Dashdyeva, G.B., and Yusibov, Yu.A., Homogeneity ranges and thermodynamic properties of ternary phases in the SnTe−

Bi$_2$Te$_3$–Te system, *Inorg. Mater.*, 2011, vol. 47, no. 3, pp. 235−239.

10. Babanly, M.B., Shevel'kov, A.V., Guseinov, F.N., and Babanly, D.M., PbTe−Bi$_2$Te$_3$−Te system studied by emf measurements, *Inorg. Mater.,* 2011, vol. 47, no. 7, pp. 712−716.

11. Elagina, E.I. and Abrikosov, N.Kh., Systems PbTe−Bi$_2$Te$_3$ and SnTe−Sb$_2$Te$_3$, *Zh. Neorg. Khim.,* 1959, vol. 4, no. 7, pp. 1638−1642.

12. Stegherr, A., Das Dreistoffsystem Zinn−Antimon−Tellur, *Philips Res. Rep., Suppl.,* 1969, vol. 24, no. 6.

13. Zhukova, T.B. and Zaslavskii, A.A., Crystal structures of the compounds PbBi$_4$Te$_7$, PbBi$_2$Te$_4$, SnBi$_4$Te$_7$, SnBi$_2$Te$_4$, SnSb$_2$Te$_4$, and GeBi$_4$Te$_7$, *Kristallografiya,* 1971, vol. 16, no. 5, pp. 918−922.

14. *Binary Alloy Phase Diagrams,* Massalski, T.B., Ed., Materials Park: ASM International, 1990, 2nd ed.

15. Morachevskii, A.G., Voronin, G.F., Geiderikh, V.A., and Kutsenok, I.B., *Elektrokhimicheskie metody issledovaniya v termodinamike metallicheskikh sistem* (Electrochemical Characterization Techniques in Thermodynamic Studies of Metallic Systems), Moscow: Akademkniga, 2003.

16. Babanly, M.B. and Yusibov, Yu.A., *Elektrokhimicheskie metody v termodinamike neorganicheskikh sistem* (Electrochemical Characterization Techniques in Thermodynamic Studies of Inorganic Systems), Baku: ELM, 2011.

17. Gordon, A.J. and Ford, R.A., *A Handbook of Practical Data, Techniques, and References,* New York: Wiley, 1972.

18. Kubaschewski, O., Alcock, C.B., and Spenser, P.J., *Materials Thermochemistry,* Oxford: Pergamon, 1993.

19. *Baza dannykh termicheskikh konstant veshchestv* (Thermal Constants of Substances Database), Yungman, V.S., Ed., 2006. http://www/chem.msu.su/cgi-bin/tkv.

20. Gerasimov, Ya.I., Krestovnikov, A.N., and Gorbov, S.I., *Khimicheskaya termodinamika v tsvetnoi metallurgii: Spravochnik* (Chemical Thermodynamics in Nonferrous Metallurgy: A Handbook), Moscow: Metallurgiya, 1974, vol. 6.

21. Melekh, B.T., Semenkovich, S.A., and Andreev, A.A., *Thermodynamic properties of group IV-A and V-A sulfides, selenides, and tellurides, in Termodinamicheskie svoistva intermetallicheskikh faz* (Thermodynamic Properties of Intermetallic Phases), Kiev: Inst. Problem Materialovedeniya, 1982, pp. 73−87.

22. Babanly, M.B., Yusibov, Yu.A., and Abishev, V.T., *Metod EDS v termodinamike slozhnykh poluprovodnikovykh veshchestv* (EMF Measurements in Thermodynamic Studies of Multicomponent Semiconductors), Baku: Bakinsk. Gos. Univ., 1992.