

THERMODYNAMIC PROPERTIES OF $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$

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Abstract. The Pb–Sb–Se system was investigated in the $\text{PbSe–Pb}_6\text{Sb}_6\text{Se}_{17}\text{–Sb}_2\text{Se}_3\text{–Se}$ composition area and temperature range 300–450 K using EMF measurements on reversible concentration cells of the type



It was shown that this subsystem consists of two three-phase regions, limited by the $\text{Pb}_6\text{Sb}_6\text{Se}_{17}\text{–Se}$ tie-line. Partial thermodynamic functions of PbSe and lead in three-phase $\text{Pb}_6\text{Sb}_6\text{Se}_{17}\text{–Sb}_2\text{Se}_3\text{–Se}$ region are calculated from the equations for the EMF temperature dependences. The standard Gibbs energy of formation, standard enthalpy of formation and standard entropy of the $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$ compound were calculated based these data and using the thermodynamic functions for PbSe and Sb_2Se_3 .

Keywords: lead-antimony selenides, $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$, EMF method, thermodynamic properties.

INTRODUCTION

Chalcogenides of heavy metals and complex phases based on them are the most promising thermoelectric materials. In particular, the phases of the LAST family (lead, antimony, silver, tellurium) and the tetradimite-like compounds of $\text{A}^{\text{IV}}\text{B}^{\text{V}}_2\text{Te}_4$, $\text{A}^{\text{IV}}\text{B}^{\text{V}}_4\text{Te}_7$, $\text{A}^{\text{IV}}\text{B}^{\text{V}}_6\text{Te}_{10}$ -type etc. ($\text{A}^{\text{IV}}\text{–Ge, Sn, Pb; B}^{\text{V}}\text{–Sb, Bi}$), due to their complex structures and lower values of the lattice component of heat conductivity in comparison with the initial binary compounds $\text{A}^{\text{IV}}\text{Te}$ and B_2Te_3 , have high thermoelectric efficiency [1–5]. In addition, recent studies have shown that many of these compounds are also three-dimensional topological insulators and can be used in spintronics and quantum computing [6–8].

In order to develop modern preparative methods and growth of single crystals of complex materials, it is necessary to investigate phase relationships and thermodynamic properties of the respective systems.

Taking this into account, we undertook a thermodynamic study of ternary compounds formed in the $\text{A}^{\text{IV}}\text{–B}^{\text{V}}\text{–X}$ (X–Se, Te) systems by the electromotive force (EMF) method. The results of a complex study of solid-phase equilibria in the systems $\text{PbSe–Bi}_2\text{Te}_3\text{–Se}$, $\text{SnTe–Sb}_2\text{Te}_3\text{–Te}$, $\text{SnTe–Bi}_2\text{Te}_3\text{–Te}$, and $\text{PbTe–Bi}_2\text{Te}_3\text{–Te}$ as well as the standard thermodynamic functions of the compounds and solid solutions formed in them are presented by us [9–12].

In this paper, we continued to study similar systems and presented the results of a thermodynamic

study of the compound $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$ by using the EMF method with glycerol electrolyte. This modification of the EMF method is successfully used for the thermodynamic study of binary and more complex metallic, semiconductor and other systems [13, 14].

Phase equilibria in the Pb–Sb–Se ternary system have been studied in a number of papers [15–17]. The phase diagram of the quasi-binary section $\text{PbSe–Sb}_2\text{Se}_3$ is presented in [15, 16]. According to [15], the PbSb_2Se_4 compound with congruent melting at 891 K formed in the system. According to [16], the system is characterized by the formation of $\text{Pb}_2\text{Sb}_2\text{Se}_5$ compound with incongruent melting at 857 K also. A recently published paper [17] presents the projection of the liquidus surface and the isothermal section at 400 K of the Pb–Sb–Se system. The existence of three ternary compounds PbSb_2Se_4 , PbSb_5Se_6 and $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$ is shown. According to the results of [17], the latter compound forms conodes with binary compounds PbSe , Sb_2Se_3 , and also elementary selenium, which leads to the formation on the phase diagram of three-phase regions $\text{PbSe–Pb}_6\text{Sb}_6\text{Se}_{17}\text{–Se}$ and $\text{Pb}_6\text{Sb}_6\text{Se}_{17}\text{–Sb}_2\text{Se}_3\text{–Se}$.

The crystal structures of lead-antimony selenides were studied in [18–21].

EXPERIMENTAL PART

For the experiments, PbSe and Sb_2Se_3 binary compounds were first synthesized. These compounds melt congruently at 1352 and 863 K [22]. Therefore, they

easily crystallize from melts of stoichiometric compositions. Synthesis was carried out by melting of elementary components of high purity in evacuated ($\sim 10^{-2}$ Pa) quartz ampoule at a temperature slightly higher (20–30 K) of melting points. The synthesis of PbSe was performed in the inclined two-zone furnace because of a high vapor pressure of elemental selenium at high temperature. The temperature of the hot zone was 1370 K, and cold 900 K (lower than the boiling point of selenium (958 K) [23]).

The alloys of the Pb–Sb–Se system were prepared by melting from the synthesized and identified starting compounds and elemental selenium. The phase compositions of the alloys were chosen using the solid-phase equilibrium diagram (Fig. 1), constructed based on data of [17]. From the each three-phase regions $\text{PbSe}-\text{Pb}_6\text{Sb}_6\text{Se}_{17}-\text{Se}$ и $\text{Pb}_6\text{Sb}_6\text{Se}_{17}-\text{Sb}_2\text{Se}_3-\text{Se}$ three alloys were prepared. Taking into account the importance of the equilibrium of electrode-alloys, the cast samples were annealed at 700 K (about 500 h) and then at 450 K (200 h). The phase compositions of the annealed alloys were controlled by the XRD method using Bruker D8 ADVANCE diffractometer (Cu K_α radiation)

For a thermodynamic study, concentration chains of the type

(–) $\text{PbSe (s)} \mid \text{liquid electrolyte, Pb}^{2+} \mid \text{Pb-Sb-Se (s)} (+) (1)$ were assembled, because concentration chains relative to the lead electrode turned out to be irreversible – the EMF values continuously decreased during the experiments. Apparently, this is due to the chemical interaction between the electrodes through the electrolyte, leading to a change in their composition.

Electrodes of chains of the type (1) were prepared by pressing PbSe (left electrode) and annealed alloys from the above-mentioned phase regions (right electrodes) in the form of tablets with a diameter of ~ 0.8 –1 cm and a thickness of 0.4–0.6 cm.

The electrolyte was a glycerol solution of KCl with addition PbCl_2 . Because the presence of either moisture or oxygen in the electrolyte was inadmissible, an-

alytically pure glycerol was thoroughly dewatered and degassed by evacuation at ~ 400 K, anhydrous chemically pure KCl and PbCl_2 were used.

The assembly of an electrochemical cell and measurements are described in detail [13, 14]. EMF measurements were done in the temperature range of 300–450 K with the accuracy of ± 0.1 mV using the high-resistance universal B7-34A digital voltmeter.

RESULTS

The results of EMF measurements were in accordance with Fig. 1 [17], according to which three-phase regions $\text{PbSe}-\text{Pb}_6\text{Sb}_6\text{Se}_{17}-\text{Se}$ and $\text{Pb}_6\text{Sb}_6\text{Se}_{17}-\text{Sb}_2\text{Se}_3-\text{Se}$ exist in the Pb-Sb-Se system in the subsolidus. We obtained two series of EMF values that corresponded to these regions.

In the three-phase region of $\text{PbSe}-\text{Pb}_6\text{Sb}_6\text{Se}_{17}-\text{Se}$, the EMF values were close to zero (2–5 mV). This is due to the presence of the PbSe phase in both electrodes. For thermodynamic calculations, the results of EMF measurements in the three-phase region $\text{Pb}_6\text{Sb}_6\text{Se}_{17}-\text{Se}$ were used. As can be seen from Fig. 2, the EMF dependences on temperature in this phase region are linear. Accordingly, the linear least-square

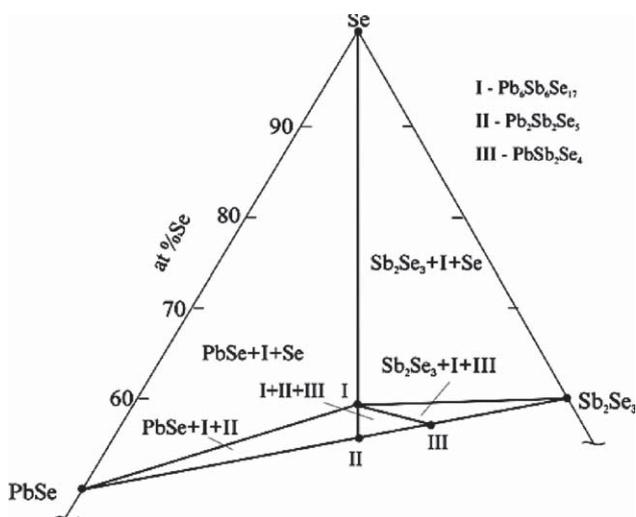


Fig. 1. Solid-phase equilibria diagram of the $\text{PbSe}-\text{Sb}_2\text{Se}_3-\text{Se}$ system

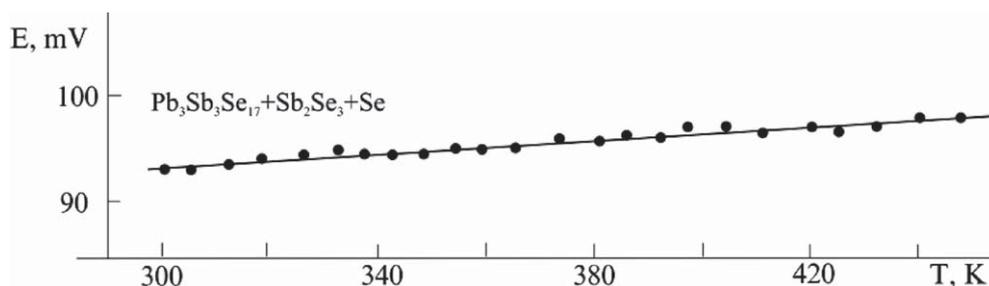


Fig. 2. EMF dependences on temperature for $\text{Pb}_6\text{Sb}_6\text{Se}_{17}-\text{Sb}_2\text{Se}_3-\text{Se}$ three-phase alloys

treatment of the data was performed and the results were expressed according to the literature recommendations [13] as:

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

where n is the number of pairs of E and T values; S_E is the error variance of the EMF readings; T is the mean absolute temperature; t is the Student's test. At the confidence level of 95 % and $n \geq 20$, the Student's test is $t \leq 2$. The experimental data of T_i and E_i and steps of calculation are presented in Table 1.

From received equation

$$E, \text{ mV} = 83.60 + 0.032T \pm 2 \left[\frac{0.48}{24} + 1.1 \cdot 10^{-5} (T - 374.3)^2 \right]^{1/2}$$

by using well known thermodynamic expressions, the partial molar functions of PbSe "component" in the alloys at 298 K were calculated

$$\begin{aligned} \overline{\Delta G}_{\text{PbSe}} &= -17.95 \pm 0.11 \text{ kJ}\cdot\text{mol}^{-1}, \\ \overline{\Delta H}_{\text{PbSe}} &= -16.13 \pm 0.48 \text{ kJ}\cdot\text{mol}^{-1}, \\ \overline{\Delta S}_{\text{PbSe}} &= 6.10 \pm 1.28 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}. \end{aligned}$$

These functions are the difference of the partial molar values of lead in PbSe and $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$:

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

where $\overline{\Delta Z}'_{\text{Pb}}$ and $\overline{\Delta Z}_{\text{Pb}}$ are the partial thermodynamic functions of lead in PbSe and $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$, respectively.

On the other hand, because the PbSe is the only compound in the Pb–Se system [22], the following relation is valid for it [14]

$$\overline{\Delta Z}'_{\text{Pb}} = \Delta_f Z^0(\text{PbSe}), \quad (4)$$

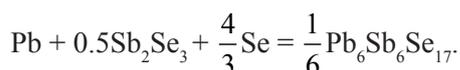
By combining relations (3) and (4) we obtain

$$\overline{\Delta Z}_{\text{Pb}} = \overline{\Delta Z}_{\text{PbSe}} + \Delta_f Z^0(\text{PbSe}). \quad (5)$$

According to [13, 14], and Fig.1, the functions $\overline{\Delta Z}_{\text{Pb}}$ in the PbSe– $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$ –Se three-phase region are the thermodynamic functions of the following potential-forming reaction:

Table 1. The experimental data of T_i and E_i and steps of calculation for the phase region $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$ –Se of the Pb–Sb–Se system

| $T_i, \text{ K}$ | $E_i, \text{ mV}$ | $T_i - \bar{T}$ | $E_i(T_i - \bar{T})$ | $(T_i - \bar{T})^2$ | \tilde{E} | $E_i - \tilde{E}$ | $(E_i - \tilde{E})^2$ |
|--------------------|-------------------|-----------------|-------------------------------------|-------------------------------------|-------------|-------------------|------------------------------------|
| 302.6 | 93.2 | -71.67 | -6679.33 | 5136.11 | 93.17 | 0.03 | 0.00 |
| 310.1 | 93.5 | -64.17 | -5999.58 | 4117.36 | 93.41 | 0.09 | 0.01 |
| 315.5 | 93.8 | -58.77 | -5512.31 | 3453.52 | 93.58 | 0.22 | 0.05 |
| 320.2 | 93.1 | -54.07 | -5033.61 | 2923.20 | 93.73 | -0.63 | 0.39 |
| 328.7 | 94.8 | -45.57 | -4319.72 | 2076.32 | 94.00 | 0.80 | 0.65 |
| 336.8 | 94.3 | -37.47 | -3533.11 | 1403.75 | 94.25 | 0.05 | 0.00 |
| 341.5 | 93.1 | -32.77 | -3050.58 | 1073.65 | 94.40 | -1.30 | 1.69 |
| 347.4 | 94 | -26.87 | -2525.47 | 721.82 | 94.59 | -0.59 | 0.35 |
| 353.3 | 95.9 | -20.97 | -2010.70 | 439.60 | 94.77 | 1.13 | 1.27 |
| 358 | 95.1 | -16.27 | -1546.96 | 264.60 | 94.92 | 0.18 | 0.03 |
| 367.3 | 95.5 | -6.97 | -665.32 | 48.53 | 95.22 | 0.28 | 0.08 |
| 372.6 | 95.8 | -1.67 | -159.67 | 2.78 | 95.38 | 0.42 | 0.17 |
| 377.5 | 95.7 | 3.23 | 309.43 | 10.45 | 95.54 | 0.16 | 0.03 |
| 381.7 | 95.3 | 7.43 | 708.40 | 55.25 | 95.67 | -0.37 | 0.14 |
| 387.1 | 95 | 12.83 | 1219.17 | 164.69 | 95.84 | -0.84 | 0.71 |
| 395.8 | 97.5 | 21.53 | 2099.50 | 463.68 | 96.12 | 1.38 | 1.91 |
| 401.3 | 96 | 27.03 | 2595.20 | 730.80 | 96.29 | -0.29 | 0.09 |
| 406.6 | 96.8 | 32.33 | 3129.87 | 1045.44 | 96.46 | 0.34 | 0.12 |
| 410.4 | 95.9 | 36.13 | 3465.19 | 1305.62 | 96.58 | -0.68 | 0.46 |
| 419.7 | 95.2 | 45.43 | 4325.25 | 2064.19 | 96.87 | -1.67 | 2.80 |
| 425.2 | 97.7 | 50.93 | 4976.19 | 2594.20 | 97.05 | 0.65 | 0.42 |
| 434.5 | 97.5 | 60.23 | 5872.75 | 3628.05 | 97.34 | 0.16 | 0.02 |
| 440.4 | 97.8 | 66.13 | 6467.84 | 4373.62 | 97.53 | 0.27 | 0.07 |
| 448.2 | 98 | 73.93 | 7245.47 | 5466.14 | 97.78 | 0.22 | 0.05 |
| $\bar{T} = 374.26$ | $\bar{E} = 95.44$ | | $\sum E_i(T_i - \bar{T}) = 1377.89$ | $\sum (T_i - \bar{T})^2 = 43563.41$ | | | $\sum (E_i - \tilde{E})^2 = 11.51$ |



According to this relation, the standard thermodynamic functions of formation of the Pb₆Sb₆Se₁₇ compound may be calculated as

$$\begin{aligned} \Delta_f Z^0(\text{Pb}_6\text{Sb}_6\text{Se}_{17}) &= 6\overline{\Delta Z}_{\text{Pb}} + 3\Delta_f Z^0(\text{Sb}_2\text{Se}_3) \quad (6) \\ (Z \equiv G, H) \text{ while standard entropy} \\ S^0(\text{Pb}_6\text{Sb}_6\text{Se}_{17}) &= \\ &= 6\overline{\Delta S}_{\text{Pb}} + 6S^0(\text{Pb}) + 3S^0(\text{Sb}_2\text{Se}_3) + 2S^0(\text{Se}). \quad (7) \end{aligned}$$

In calculations we used literature data on the relevant thermodynamic data on PbSe and Sb₂Se₃ (Table 2) and the standard entropies of lead ($64.81 \pm 0.21 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and selenium ($42.13 \pm 0.21 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) presented in Ref. [24]. The standard integral thermodynamic functions of PbSe and Sb₂Se₃ used in our calculations are self consistent and quite reliable. The standard heats of formation and standard entropies recommended in several handbooks and review articles [24–27] 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 obtained from EMF measurements [26–28].

As a result of the calculations by relation (5), we obtained the following partial molar functions of the lead in Pb₆Sb₆Se₁₇

$$\begin{aligned} \overline{\Delta G}_{\text{Pb}} &= -114.45 \pm 3.11 \text{ kJ}\cdot\text{mol}^{-1}, \\ \overline{\Delta H}_{\text{Pb}} &= -116.13 \pm 2.58 \text{ kJ}\cdot\text{mol}^{-1}, \\ \overline{\Delta S}_{\text{Pb}} &= -5.63 \pm 3.38 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}. \end{aligned}$$

The standard integral thermodynamic functions of the Pb₆Sb₆Se₁₇ calculated using relations (6) and (7) and thermodynamic data of the binary compounds (Table 2). The estimated standard deviations were calculated by accumulating the errors.

CONCLUSION

By using the EMF method the self-consistent data on the standard integral thermodynamic functions of the Pb₆Sb₆Se₁₇, which is interest as a thermoelectric material are obtained.

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Table 2. Standard integral thermodynamic functions of PbSe, Sb₂Se₃, and Pb₆Sb₆Se₁₇

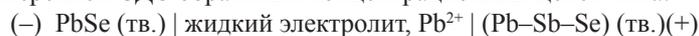
| Compound | $-\Delta_f G^0(298 \text{ K})$ | $-\Delta_f H^0(298 \text{ K})$ | $S^0(298 \text{ K}), \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ |
|--|--------------------------------|--------------------------------|---|
| | kJ·mol ⁻¹ | | |
| PbSe | 96.5±3.0 | 100.0±2.1 [24, 25] | 102.5±2.1 [24, 25] |
| Sb ₂ Se ₃ | 125.9±3.0 | 127.6±1.3 [25, 26] | 212.1±3.3 [25, 26] |
| Pb ₆ Sb ₆ Se ₁₇ | 1064±28 | 1080±20 | 1387±35 |

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ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА $Pb_6Sb_6Se_{17}$ © 2017 Ш. Г. Мансимова¹, Э. Н. Оруджлу², С. Г. Султанова¹, М. Б. Бабанлы²¹Бакинский государственный университет, ул. Академика Захида Халилова, 23, AZ 1148 Баку, Азербайджан²Институт катализа и неорганической химии НАНА, пр. Г. Джавида, 113, AZ 1143 Баку, Азербайджан
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Аннотация. Измерением ЭДС обратимых концентрационных цепей типа:

в интервале температур 300–450 К исследована система Pb–Sb–Se в области составов $PbSe-Pb_6Sb_6Se_{17}-Sb_2Se_3-Se$. Показано, что эта подсистема состоит из двух трехфазных областей, разделенных коннодой $Pb_6Sb_6Se_{17}-Se$. Из данных измерений ЭДС для трехфазной области $Pb_6Sb_6Se_{17}-Sb_2Se_3-Se$ получено линейное уравнение типа $E = a + bT \pm tS_E(T)$, с использованием которого вычислены парциальные термодинамические функции PbSe в сплавах. Комбинированием этих данных с термодинамическими функциями образования PbSe рассчитаны парциальные термодинамические функции свинца. На основании полученных данных и диаграммы твердофазных равновесий подсистемы $PbSe-Pb_6Sb_6Se_{17}-Sb_2Se_3-Se$ с использованием соответствующих термодинамических функций Sb_2Se_3 рассчитаны стандартные свободная энергия Гиббса образования и энтальпия образования, а также стандартная энтропия соединения $Pb_6Sb_6Se_{17}$.

Ключевые слова: система Pb-Sb-Se, $Pb_6Sb_6Se_{17}$, метод ЭДС, термодинамические свойства.

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