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Abstract

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PHYSICOCHEMICAL ANALYSIS OF BINARY SYSTEMS OF TELLURIUM WITH ELEMENTS OF THE GERMANIUM SUBGROUP IN THE LIQUID STATE

(Presented by Academician I. V. Tananaev, 11 XI 1964)

Phase equilibria in the binary systems Ge—Te, Sn—Te, and Pb—Te are characterized by state diagrams with one chemical compound of the type A^{IV}Te (where A^{IV}—Ge, Sn, Pb) (^{1,2}). These compounds are distinguished by valuable electrical properties and in recent years have found practical application as materials for thermoelements. In this connection, a comprehensive study of the features of chemical interaction in the indicated systems at high temperatures in the liquid state is of interest, with the aim of elucidating the thermal stability of the compounds A^{IV}Te above the melting temperature.

With respect to germanium telluride this is of particular interest, since from the available data on the Ge—Te state diagram it is still unclear whether this compound is formed by a peritectic reaction or melts congruently.

To solve the problem posed in this work, the method of physicochemical analysis developed in the works of N. S. Kurnakov was employed, involving the construction of chemical composition—property diagrams (^{3,4}). For the investigation, alloys were prepared* whose composition is given in Table 1.

Table 1

Chemical composition of the investigated alloys

Ge—Te	Ge—Te	Ge—Te	Sn—Te	Sn—Te	Sn—Te	Pb—Te	Pb—Te	Pb—Te
Alloy no.	Te, at. %	Ge, at. %	Alloy no.	Te, at. %	Sn, at. %	Alloy no.	Te, at. %	Pb, at. %
1	10	90	1	20	80	1	10	90
2	20	80	2	35	65	2	35	65
3	35	65	3	45	55	3	45	55
4	45	55	4	48.5	51.5	4	48.5	51.5
5	48.5	51.5	5	50	50	5	50	50
6	50	50	6	51.5	48.5	6	51.5	48.5

Fig. 1. Isotherms of viscosity and electrical conductivity of melts in the Ge—Te system: 1 —730°; 2 —750°; 3 —800°; 4 —800°; 5 —850°; 6 —900°.

Figure 1: Fig. 1. Isotherms of viscosity and electrical conductivity of melts in the Ge—Te system: 1 —730°; 2 —750°; 3 —800°; 4 —800°; 5 —850°; 6 —900°.

Fig. 2. Isotherms of viscosity and electrical conductivity of melts in the Sn—Te system: 1 —800°; 2 —900°; 3 —1000°; 4 —1100°; 5 —1150°.

Figure 2: Fig. 2. Isotherms of viscosity and electrical conductivity of melts in the Sn—Te system: 1 —800°; 2 —900°; 3 —1000°; 4 —1100°; 5 —1150°.

Ge—Te	Ge—Te	Ge—Te	Sn—Te	Sn—Te	Sn—Te	Pb—Te	Pb—Te	Pb—Te
7	50.6	49.4	7	55	45	7	55	45
8	51.5	48.5	8	65	35	8	65	35
9	55	45	9	80	20	9	75	25
10	65	35	10	90	10	10	85.5	14.5
11	80	20						
12	90	10						

As starting materials for preparing the alloys, tellurium, germanium, tin, and lead of high purity were used.**

The alloys were prepared in quartz ampoules evacuated to 10^{-3} mm Hg; in the case of the Pb—Te system these ampoules were coated on the inside with a mirror layer of pyrocarbon, applied by the method described in (5).

As methods for the investigation, viscosity and electrical conductivity were chosen, which, in the opinion of N. S. Kurnakov and a number of other investigators, are respectively structure- and bond-sensitive properties. All measurements were carried out on the high-temperature vacuum apparatus described in (6). The procedure for conducting experiments of this type has been described in detail in a number of previously published works (7, 8).

Fig. 1. Isotherms of viscosity and electrical conductivity of melts in the Ge—Te system:
1 —730°; 2 —750°; 3 —800°;
4 —800°; 5 —850°; 6 —900°.

Fig. 2. Isotherms of viscosity and electrical conductivity of melts in the Sn—Te system:

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* O. V. Situlina participated in carrying out the experiments on the Sn—Te and Pb—Te systems.

** Tellurium after double distillation in vacuum; germanium with a purity of $\sim 10^{13}$ cm^{-3}; lead (99.997% Pb) and tin (99.994% Sn).

Figure 3

Figure 3: Figure 3

1 –800°; 2 –900°; 3 –1000°;
4 –1100°; 5 –1150°.

Measurements were made in the temperature range up to 1200°. As a result of the measurements, curves of the temperature dependence* of viscosity and electrical conductivity were constructed for all alloys listed in Table 1. From these curves, isotherms of the indicated properties were constructed, characterizing the general nature of the chemical interaction; these are presented in Figs. 1-3 in comparison with the equilibrium phase diagrams. From the graphs shown it follows that the chemical diagrams viscosity–composition and electrical conductivity–composition are distinguished by the presence, respectively, of a maximum and a minimum located, in composition, near the compounds GeTe, SnTe, and PbTe.

* Each curve was constructed on the basis of at least 10–15 points. The curves for compounds A^{IV}Te and alloys close to them in composition were constructed from 20–30 points obtained on different samples in several experiments.

On the basis of an analysis of the nature of these dependences at different temperatures, one can draw certain conclusions about the thermal stability of germanium, tin, and lead tellurides, using the basic regularities of physicochemical analysis established in the works of N. S. Kurnakov (3, 4).

It follows from Figs. 1 and 2 that the minimum of electrical conductivity and the maximum of viscosity on the isotherms in the germanium–tellurium and tin–tellurium systems are not singular, which indicates dissociation of germanium and tin tellurides directly upon melting. The minimum on the electrical-conductivity isotherms in the germanium–tellurium and tin–tellurium systems is shifted in composition toward tellurium, which in the liquid state has a considerably lower electrical conductivity than germanium and tin. This shift fully conforms to the regularities established by N. S. Kurnakov for markedly dissociating compounds formed by components whose electrical conductivities differ substantially.

Fig. 3. Isotherms of viscosity and electrical conductivity of melts in the Pb–Te system: **1** –950°; **2** –1000°; **3** –1100°; **4** –1150°; **5** –1200°.

The maximum on the viscosity isotherms in the germanium–tellurium system is diffuse and shifted toward the more viscous tellurium; moreover, with increasing temperature the maximum becomes increasingly diffuse and shifts in the indicated direction, which also fully agrees with the regularities of physicochemical analysis. A corresponding shift on the curves of the concentration dependence of viscosity in the tin–tellurium system is not observed, which apparently may be explained by the insignificant difference in the viscosity of tin and tellurium in the temperature interval investigated (9, 10).

With respect to the general character of the chemical interaction in the Ge—Te system, on the basis of the data obtained one can draw one further important conclusion. The presence of an extremum on chemical composition—property diagrams in the liquid state unambiguously proves the congruent character of melting of germanium telluride, since in the case of incongruent melting the composition—property diagrams are characterized by smooth curves. Evidently, at 725° an eutectic transformation of the type $L \rightarrow \alpha + \mathrm{GeTe}$ takes place, the eutectic being pronounced, or germanium telluride melts congruently at a transition point*.

In the Pb—Te system, the viscosity and electrical-conductivity isotherms at 950° differ by the presence of clearly expressed singular points corresponding in composition to the compound PbTe, which testifies to the relative thermal stability of this compound at the melting temperature and with some superheating. In any case, it can be stated with sufficient certainty that the degree of dissociation of lead telluride upon melting is insignificant. Upon further heating, the character of the isotherms changes.

* The possibility of the existence of this type of compound was proved in the work of I. I. Novikov by the method of geometrical thermodynamics ([11]).

The extrema on the viscosity isotherms become blurred; on this basis it may be concluded that lead telluride undergoes significant dissociation upon superheating already by 50-70° relative to the melting temperature.

The experimental data obtained should be taken into account in developing processes for the synthesis and purification of these compounds by crystallization methods.

In particular, in order to preserve the stoichiometric ratio between the components in the melt of the compounds GeTe and SnTe, it is necessary to create above the melt an equilibrium vapor pressure of tellurium at the corresponding temperature, analogous to what is done in the case of compounds $A^{\mathrm{III}}P$ or $A^{\mathrm{III}}As$. With respect to lead telluride, in the indicated processes it is necessary to monitor the temperature regime carefully, remaining within the interval of thermal stability of this compound.

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