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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF GALLIUM TELLURIDES BY THE ELECTROMOTIVE-FORCE METHOD

The phase diagram of the gallium–tellurium system, given in the monograph by Hansen and Anderko (^{1}), indicates the existence of compounds of composition Ga_2Te_3 and GaTe without homogeneity ranges.

It is also noted there that the structure of the tellurium-rich region has not been fully elucidated, but the formation in it of a telluride of composition $GaTe_3$ is assumed.

A subsequent work by Newman (^{2}) confirmed the existence of the tellurides Ga_2Te_3 and GaTe, and also showed that two others exist–Ga_3Te_2 and $GaTe_3$, which are not stable at room temperature. In Fig. 1 (the diagram according to (^{2})) this situation is indicated by dashed lines. Recently, a study of the gallium–tellurium system by metallographic methods was published (^{3}): microstructure, microhardness, and X-ray phase analysis. The results of the work confirmed the presence in the system of phases of composition Ga_2Te_3 and GaTe; the author ascribes to the Ga_2Te_3 phase a certain region of extent less than 0.3 at.% toward gallium.

Fig. 1

The phase of composition Ga_3Te_2 was not detected at all in this investigation. The stability of the telluride of composition $GaTe_3$ at room temperature was proved only on a crystalline specimen, while a specimen ground into powder gave no lines of the $GaTe_3$ phase on Debye diagrams.

The aim of our investigation was to study the thermodynamic properties of gallium tellurides. Gallium monotelluride GaTe possesses semiconducting properties (^{4}).

The telluride of composition Ga_2Te_3 belongs to the group of semiconductor compounds of the type $A_2^{III}B_3^{VI}$, characterized by a defective sphalerite structure (^{5,6}).

The recently increased interest in the study of semiconductors of the group $A_2^{III}B_3^{VI}$ is due to the fact that, because of their low thermal conductivity, they may be used in thermoelectricity; and the presence of defects in them makes it possible to trace the influence of the latter and of their ordering on physicochemical and electrical properties.

In the present work the electromotive-force method was employed, the procedure of which is described in (^{7,8}).

Concentration (relative to the electrodes) electrochemical cells of the following type were studied:

$$(-)\mathrm{Ga}_{(\ell)} \mid \text{liquid electrolyte} + \mathrm{GaCl}_3 \mid (\mathrm{Ga}_x\mathrm{Te}_{1-x})^{(+)}_{(\text{solid})},$$

where x is the mole fraction of gallium.

The principal thermodynamic functions (ΔG, ΔS, and ΔH) were calculated from the equations:

$$\Delta G = -zFE, \tag{1}$$

where ΔG is the isobaric-isothermal Gibbs potential, z is the charge of the gallium ion, equal to 3*, F is the Faraday number, equal to 23 062 cal/V · g-equiv, and E is the e.m.f. in volts.

$$\Delta S = -\frac{d(\Delta G)}{dT} = zF\frac{dE}{dT}, \tag{2}$$

$$\Delta H = \Delta G + T\Delta S. \tag{3}$$

For the preparation of the electrodes, gallium of 99.999% purity and tellurium purified by sublimation, not less than 99.99%, were used.

The alloys were prepared by melting the components in evacuated quartz ampoules with subsequent prolonged annealing (not less than 50 hours).

The phases were identified by X-ray phase analysis both for stoichiometric compositions and for intermediate alloys. The photographs were taken by the powder method in an RKD-57 camera using CuK_α–K_β radiation. In analysis of an alloy of composition 65.1 at.% Te, lines of Ga_2Te_3 and tellurium were found; no lines of GaTe were detected.

The parameters found agree well with the literature data (^{5,10}):
Ga_2Te_3: $a = 5.89$ Å; GaTe: $a = 23.79$ Å, $b = 4.08$ Å, $c = 10.49$ Å, $\beta = 45.7°$.

The electrolyte in the cells was a ternary mixture of chlorides: $ZnCl_2$—70, KCl —18, NaCl—12 wt.% with a melting point of 206°.

Gallium chloride—$GaCl_3$—was added to the melt in a small amount. The composition of the alloys after the experiments was checked by chemical analysis. The construction of the cells is described in (^{11}).

Alloys of compositions 53.2-84.2 at.% Te were investigated. As the results showed, all alloys of compositions 63.5-84.2 at.% Te gave a constant e.m.f. value within the experimental error of ±11.0 mV.

This means that the alloys studied lie in one and the same phase field. On the basis of the X-ray phase-analysis data (see above, analysis of the alloy with 65.1 at.% Te), it is natural to assume that the measured e.m.f.' s correspond to two-phase alloys Ga_2Te_3—Te; consequently, under the conditions of our experiment the telluride $GaTe_3$ is not formed.

Alloys of compositions 53.2-55.7 at.% Te also gave a constant e.m.f. value, which corresponds to the formation of the GaTe phase from Ga_2Te_3 and gallium.

As a result of processing, by the method of least squares, the experimental data referring to all experiments with all alloys separately for each region, equations were found for the dependence of the e.m.f. on the absolute temperature in the form $E = A + BT$.

The errors of the e.m.f. values, as well as of the coefficients of the equation A and B, which characterize the accuracy of determination of the heats and entropies of formation, were calculated using the formulas of the least-squares method (^{12}). The measurement results are summarized in Table 1.

Table 1

Phase region	Reaction	Temperature interval	$E = f(T)$, V
Ga_2Te_3—Te	$Ga_{(l)} + 1.5Te_{(s)} == 0.5Ga_2Te_3$	563-653° K	$0.5939 - 0.2490 \cdot 10^{-3}T$
Ga_2Te_3—GaTe	$Ga_{(l)} + Ga_2Te_3 == 3GaTe$	543-673° K	$0.2026 - 0.1860 \cdot 10^{-3}T$

Calculation of the principal thermodynamic functions of formation of Ga_2Te_3 and GaTe from the pure components (liquid gallium and solid tellurium) was carried out by combining the equations $E = f(T)$ obtained for each region and relation (1).

* In work (^{9}) it was shown that the charge of gallium is equal to 3.

The recalculation of the experimental data to standard values (298° K) was carried out using the heat capacity of the compound Ca_2Te_3 ([13]), of gallium ([14]), of tellurium ([15]), and the heat of fusion of gallium ([15]).

In the case of gallium monotelluride, because of the absence of data on the heat capacity of the compound, only the heat of fusion of gallium was taken into account.

Table 2

Phase	Mean 563-653° K: $-\Delta H$, kcal/mole	Mean 563-653° K: $-\Delta S$, e.u./mole	$-\Delta G$ 608°, kcal/mole	$-\Delta H^0$ 298°, kcal/mole	ΔS^0 298°, e.u./mole	$-\Delta G^0$ 298°, kcal/mole	$-\Delta H$ 298° according to ([16]), kcal/mole
Ga_2Te_3	82$±5	34±8	61.5±1.5	82±5	31±8	72±2	65±3
GaTe	32±2	15.8±3.5	22.2±0.5	30±2	11.4±2	26.5±0.5	2

The calculated values are summarized in Table 2, where the heats of formation of the tellurides according to ([16]), obtained by the combustion method in a calorimetric bomb, are also given. The results of our study and of ([16]) agree with one another for the monotelluride, while for the higher telluride there is a discrepancy. The errors of the different methods were probably involved.

It should be noted that in ([16]) no data are given on the purity and composition of the substances used, nor on the method of allowing for completeness of combustion.

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