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THERMODYNAMIC PROPERTIES OF GERMANIUM TELLURIDE

T.M. Alakbarova*

Azerbaijan State Oil and Industry University, Baku, Azerbaijan

Abstract. The Ge-Te system was studied by measuring electromotive force (EMF) of concentration cell relative to the Ge-electrode in the temperature range of 300-450 K. The partial molar functions of germanium in the alloys and the corresponding integral thermodynamic functions of the GeTe compound were calculated based on EMF measurements. The presented new thermodynamic data eliminate the contradictions and inconsistencies in the literature.

Keywords: *GeTe, EMF method, partial molar functions, thermodynamic functions.*

Corresponding Author: *Turkan Alakbarova, Azerbaijan State Oil and Industry University, Azadlig Avenue 16/21, Baku, Azerbaijan, Tel.: (+99412) 493 45 57, e-mail: turkanbdu@hotmail.com*

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1. Introduction

Germanium telluride, as well as solid solutions and doped phases based on it, are of great interest as thermoelectric, ferroelectric, and optoelectronic materials (Dangic *et al.*, 2020; Gainza *et al.*, 2019; Jin *et al*., 2019; Kriegner *et al.*, 2019; Rinaldi *et al.*, 2018; Yang *et al*., 2020). Recent studies have shown that the partial substitution of germanium by bismuth or antimony can significantly increase the thermoelectric performance of GeTe. In particular, according to (Gainza *et al.*, 2019; Jin *et al.*, 2019) in $Ge_{0.94}Bi_{0.06}Te$ solid solutions, the maximum value of ZT = 1.9 at 723 K was reached, which makes this material an excellent candidate for replacing toxic PbTe in medium-temperature thermoelectric converters. Moreover, GeTe has recently been theoretically proposed as a starting compound for a new class of functional materials - ferroelectric Rashba semiconductors (Rinaldi *et al.*, 2018). It is also known that layered germanium tellurides of antimony and bismuth exhibit topological insulator properties and are considered to be highly promising for application in quantum computers, spintronics, memory devices, security systems, etc. (Ahmad *et al.*, 2021, Nurmamat *et al.*, 2020; Okamoto *et al*., 2012).

Although GeTe and phases based on it are very important functional materials, information on the thermodynamic properties of this compound, in particular the standard thermodynamic functions of formation, is limited and contradictory with one another. There are no calorimetric results for the enthalpy of formation. The results of studies (Colin & Drowart 1964; Hirayama 1964) conducted by the vapour pressure measurements vary more than 25%. The results obtained by EMF measurements in the temperature range of 553-653 K (Sadikov & Semenkovich, 1966), which are considered more accurate by the authors of the (Gerasimov *et al.*, 1974), are also significantly different from (Colin & Drowart, 1964; Hirayama, 1964). The values of the $\Delta_f H^0$, $\Delta_f G^0$ and S^0functions given in modern databases (Barin, 2008; Iorish & Yungman, 2006; Kubaschewski *et al*. 1993) are also different from each other.

This work aims to obtain a new set of mutually agreed results related to the standard partial and integral thermodynamic functions of the GeTe compound based on EMF measurements in the low (300-450 K) temperature range. Various modifications of the EMF method are widely used in the thermodynamic study of metal chalcogenides (Babanly *et al.* 2019; Babanly & Yusibov, 2011; Mashadiyeva *et al.*, 2020a,b; Morachevskii *et al.* 2003; Moroz *et al.* 2018). Glycerol based electrolytes (Imamaliyeva *et al.* 2020a; Imamaliyeva *et al.* 2020b; Osadchii *et al.* 2016; Vassiliev *et al.* 2019; Vassiliev and Lysenko, 2016) and ionic liquid (Aliev *et al.* 2018; Hasanova *et al.* 2020a; Hasanova *et al.* 2020b; Imamaliyeva *et al.*, 2019) have been successfully used in relatively low-temperature studies.

2. Experimental

Materials and synthesis

For thermodynamic studies of the Ge-Te system, alloys with compositions 55 and 70 at% Te were prepared. The synthesis was carried out by fusion of high purity initial elemental components, purchased from Alfa Aesar in evacuated (~10^{-2}Pa) quartz ampoules at 1000K. To achieve equilibrium alloys, the samples were subjected to long-term stepwise annealing: first, the alloys were kept at 650 K (500 h), and then at 400 K (100 h).

For the experiments, concentration cells of the type

$$(-)\ Ge\ (solid)\ |\ glycerol,\ Ge^{2+}\ |\ Ge\text{-}Te\ \ (solid)\ \ (+) \qquad (1)$$

were assembled.

In the cells of type (1), the glycerol solution of KCl with the addition of 0.1 wt% $GeCl_2$ served as an electrolyte. Because the presence of either moisture or oxygen in the electrolyte was inadmissible, glycerol was thoroughly dewatered and degassed by evacuation at ~450 K, anhydrous chemically pure salts were used.

The left electrode was prepared by attaching a piece of elemental germanium to a molybdenum wire while the right electrode by pressing the powdered equilibrium alloys of the Ge-Te system in the form of pellets (diameter 5 mm and thickness 2-3 mm) in a molybdenum wire (current leads).

The used electrochemical cells had the construction of (Imamaliyeva *et al.* 2020a), which allows at the same time EMF measurements of 6–7 electrodes relative to one reference electrode. After the evacuation of air, an atmosphere of argon was created in the electrochemical cells (pressure ~300-400 mm Hg).

EMF measurements were carried out using a Keithley 2100 6 1/2 Digit Multimeter in the 300-450 K temperature range. The first equilibrium values of the EMF were obtained after keeping the electrochemical cell at ~400 K for 40-60 h, and subsequent values were taken every 3-4 hours after a certain temperature was maintained. The system was considered to be in equilibrium if the EMF measurements were constant or their variations were not significant (<0.5 mV) regardless of the direction of the temperature change at repeated measurements at a given temperature.

3. Results and Discussion

The results of EMF measurements of electrochemical cells of type (1) showed that the EMF values for both alloys (right electrodes) from the GeTe+Te two-phase area practically coincide and linearly depend on temperature (Figure 1). This allows to use

EMF data for thermodynamic calculations (Babanly & Yusibov, 2011; Morachevskii *et al.*, 2003)

Experimental data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the GeTe+Te phase area are listed in Table 1.

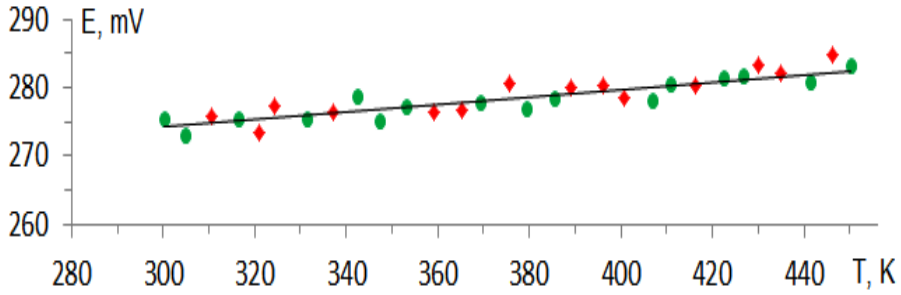

Figure1. Temperature dependences of EMF of the cells type (1) for alloys fromthe GeTe+Te two-phase area

Results of the EMF measurements were processed by the least squares method using a special computer program and linear equations of the type (2) were obtained (Morachevskii *et al.*, 2003):

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

where $n -$ is the number of pairs of values of E and T; S_E and S_b- are the variances of individual measurements of EMF and coefficient b, respectively; $\overline{\mathrm{T}}$ - average absolute temperature, Student's t-test. At the confidence level of 95% and $n = 30$, the Student's test is $t \leq 2$.

$$E,\ mv = 256.50 + 0.0586\ T \pm 2\ [\frac{1.64}{30} + 2.6 \cdot 10^{-5}(T - 376.5)^2\ ]^{1/2} \quad (3)$$

From equation (3), using thermodynamic expressions

$$\Delta\bar{G}_{Ge} = -zFE \quad (4)$$

$$\Delta\bar{H}_{Ge} = -zF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa \quad (5)$$

$$\Delta\bar{S}_{Ge} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb \quad (6)$$

the relative partial thermodynamic functions of germanium in the GeTe + Te two-phase field at 298.15 K were calculated.

$$\Delta\bar{G}_{Ge} = -52.87 \pm 0.09\ kJ/mole$$

$$\Delta\bar{H}_{Ge} = -49.50 \pm 0.38\ kJ/mole$$

$$\Delta\bar{S}_{Ge} = 11.30 \pm 1.00\ J/(K \cdot mole)$$

According to the phase diagram of the Ge-Te system, these quantities are thermodynamic functions of the following virtual-cell reaction

Ge(solid) + Te(solid) = GeTe(solid)

That is, they are standard thermodynamic functions of the formation of the GeTe compound. Standard entropy of the GeTe compound was calculated using the relation

$$S^0_{GeTe} = S^0_{Ge} + S_{Te}{}^0 + \Delta_f S^0_{GeTe}$$

During calculations, the standard entropies of elementary Ge and Te presented in the database (Iorish & Yungman, 2006) were used: $S^0_{Ge} = 31.13 \pm 0.30$ J$\cdot K^{-1} \cdot mol^{-1}$; $S^0_{Te} = 49.50 \pm 0.21$ J$\cdot K^{-1} \cdot mole^{-1}$.

The values obtained for the standard integral thermodynamic functions of the GeTe compound are given in Table 2. Table 2 alsorepresents the results of several original works and the data recommended in modern handbooks and digital databases.

Table 1. Experimental data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the GeTe+Te phase region of the Ge-Te system

T_i, K	E_i, mV	$T_i - \overline{T}$	$E_i(T_i - \overline{T})$	$(T_i - \overline{T})^2$	$\widetilde{E}$	$E_i - \widetilde{E}$	$(E_i - \widetilde{E})^2$
300.3	275.45	-76.20	-20989.29	5806.44	274.08	1.37	1.87
304.8	273.16	-71.70	-19585.57	5140.89	274.35	-1.19	1.41
310.5	275.91	-66.00	-18210.06	4356.00	274.68	1.23	1.51
316.3	275.43	-60.20	-16580.89	3624.04	275.02	0.41	0.17
320.9	273.27	-55.60	-15193.81	3091.36	275.29	-2.02	4.08
324.2	277.33	-52.30	-14504.36	2735.29	275.48	1.85	3.41
331.5	275.41	-45.00	-12393.45	2025.00	275.91	-0.50	0.25
337.3	276.42	-39.20	-10835.66	1536.64	276.25	0.17	0.03
342.4	278.91	-34.10	-9510.83	1162.81	276.55	2.36	5.57
347.4	275.14	-29.10	-8006.57	846.81	276.84	-1.70	2.90
353.2	277.33	-23.30	-6461.79	542.89	277.18	0.15	0.02
359.2	276.42	-17.30	-4782.07	299.29	277.53	-1.11	1.24
365.2	276.81	-11.30	-3127.95	127.69	277.89	-1.08	1.16
369.2	277.92	-7.30	-2028.82	53.29	278.12	-0.20	0.04
375.7	280.64	-0.80	-224.51	0.64	278.50	2.14	4.58
379.3	276.92	2.80	775.38	7.84	278.71	-1.79	3.21
385.5	278.63	9.00	2507.67	81.00	279.08	-0.45	0.20
389.2	279.91	12.70	3554.86	161.29	279.29	0.62	0.38
396.1	280.24	19.60	5492.70	384.16	279.70	0.54	0.30
400.8	278.52	24.30	6768.04	590.49	279.97	-1.45	2.11
406.7	278.15	30.20	8400.13	912.04	280.32	-2.17	4.70
410.7	280.62	34.20	9597.20	1169.64	280.55	0.07	0.00
416.4	280.16	39.90	11178.38	1592.01	280.89	-0.73	0.53
422.5	281.33	46.00	12941.18	2116.00	281.24	0.09	0.01
426.7	281.91	50.20	14151.88	2520.04	281.49	0.42	0.18
430.2	283.26	53.70	15211.06	2883.69	281.69	1.57	2.45
434.9	282.13	58.40	16476.39	3410.56	281.97	0.16	0.03
441.3	280.93	64.80	18204.26	4199.04	282.34	-1.41	2.00
446.3	284.82	69.80	19880.44	4872.04	282.64	2.18	4.76
450.3	283.35	73.80	20911.23	5446.44	282.87	0.48	0.23
$\overline{T} = 376.5$	$\overline{E} = 278.5$						

Table 2. Standard integral thermodynamic functions of GeTe

$-\Delta_fG^0$ (298K)	$-\Delta_fH^0$ (298K)	Δ_fS^0 (298K)	S^0 (298K)	References, method
kJ·mole^{-1}		J·mole^{-1}·K^{-1}		
52.87 ± 0.09	49.5 ± 0.4	11.3 ± 1.0	91.1 ± 1.4	This work, EMF (300-450K)
55.23 ± 0.21	54.34 ± 2.1	3.0 ± 2.0		Sadikov & Semenkovich, 1966, EMF (553-653K)
34.3	33.5			Hirayama, 1964, vapour pressure
	25.1			Colin & Drowart, 1964, vapour pressure
33.55	32.64 ± 14.6	3.1	83.7	Iorish & Yungman, 2006, recomended
-	48.5±10.5	-	88.9±1.0	Kubaschewski *et al*., 1993, recomended
51.33	48.53	9.4	89.96	Barin, 2008, recomended
55.2 ± 0.2	54.4±2.1		83.3± 4.0	Gerasimov *et al.*, 1974, recomended

The standard Gibbs free energy of formation of germanium telluride, determined in this work is very accurate and differ only up to~5% from the data obtained by high-temperature EMF measurements (Sadikov & Semenkovich, 1966), (Table 2). The standard enthalpy of formation of GeTe obtained by us differs from the results of (Sadikov and Semenkovich 1966), by ~ 9% and even more (up to 50%) from the values calculated from the vapour pressure measurements (Colin & Drowart, 1964; Hirayama, 1964). Comparison of our results with the values given in fundamental databases and reference books (Barin, 2008; Gerasimov *et al.*, 1974; Iorish & Yungman, 2006; Kubaschewski *et al*., 1993) shows that they are very close to the values recommended by Barin (2008) and Kubashevski *et al*. (1993). That is, for the functions Δ_fG^0 and Δ_fH^0, their difference is 2-3%, and for S^0 - only 1%. Thermodynamic data recommended in the handbook Gerasimov *et al.* (1974) are based on the results of Sadikov & Semenkovich (1966), and the data in Iorish & Yungman (2006) are based on more inaccurate results calculated based on the vapour pressure measurements (Colin & Drowart, 1964; Hirayama, 1964).

Thus, as a result of present study, a new, more reliable, mutually consistent set of standard thermodynamic functions of the GeTe compound was obtained.

4. Conclusion

This contribution presents the results of thermodynamic study of germanium telluride by means of EMF method. From the data of EMF measurements of the concentration cells type (1) in the 300-450 K temperature interval, the standard thermodynamic functions of formation and the standard entropy of GeTe were calculated. Obtained results eliminates the gap and contradictions in the thermodynamic data of germanium telluride available in the literature.

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