

THERMODYNAMIC PROPERTIES OF GdTe COMPOUND

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The results of thermodynamic investigation of GdTe investigation by the method of electromotive force (EMF) are presented in the work. The relative partial molar functions of gadolinium in GdTe+Gd₂Te₃ two-phase region are calculated from data obtained by method of rapid fixing of EMF. Gibb's standard free formation energy and formation enthalpy and also the standard entropy of GdTe compound are calculated on the base of obtained data and integral thermodynamic functions of GdTe.

Keywords: gadolinium telluride, GdTe, Gd₂Te₃, EMF method, thermodynamic functions.

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The rare-earth element chalcogenides are related to the number of perspective materials of electron technique. Many of them have the unique magnetic, optic and thermoelectric properties along with high thermostability and stability to strong changes of external conditions [1-4].

The development and optimization of new material obtaining processes are based on data on phase equilibriums in corresponding systems and thermodynamic characteristics of intermediate phases.

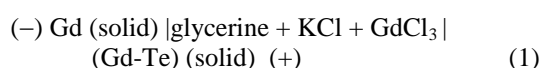
Gd-Te system [1,5] is characterized by telluride formations with GdTe, Gd₂Te₃, Gd₄Te₇, GdTe₂, Gd₂Te₅ and GdTe₃ compositions. GdTe compound congruently melts at 2098K and the rest form by peritectic reactions. The first two compounds have the cubic structure, the rest crystallize in more low-symmetry structures.

The thermodynamic properties of gadolinium tellurides aren't practically studied. Any thermodynamic data for these compounds are absent in modern reference books [6,7]. The data by standard entropy of Gd₂Te₃ are given in only electron version of "Thermal constants of substances" reference book. The standard enthalpy of this compound formation is obtained in work [8] by the method of direct synthesis from components in calorimetric bomb.

The given work is dedicated to thermodynamic properties of gadolinium monotelluride by EMF method.

EXPERIMENT AND THEIR RESULTS

The concentration chains of type



are constructed by us for study of thermodynamic properties of GdTe compound.

The melts of Gd-Te with compositions 51 and 55 at Te% (two-phase region GdTe+ Gd₂Te₃) which are synthesized by ceramic method from elementary powdery gadolinium and tellurium of high degree purity are used as right electrodes in chains of (1) type.

The synthesis is carried out in evacuated (10⁻²Pa) quartz ampoules at 1000K. Later the melts are grinded in powder, carefully mixed and pressed in tabs which are annealed at the same temperature during ~800h. The melt phase compositions are controlled by RFA method.

The left electrolyte is prepared by the fixing of [bvbxtcrb xbcnsqmetallic gadolinium on molybdenum shunt and the right electrodes are prepared by pressing-in by Gd-Te synthesized melts grinded in powder on shunts in the form of cylinder tabs of mass ~0,5gr.

KCl glycerin solution with addition of GdCl₃ serves as electrolyte. Taking into consideration the inadmissibility of the presence of humidity and oxygen in electrolyte the glycerin (by ЧДА mark) are thoroughly dehydrated and degassed by pumping at temperature ~450K and the anhydrous, chemically pure KCl an GdCl₃ are used.

However, EMF measurements show the non-equilibrium of chains by (1) type. EMF values strongly decrease in measurement beginning during several hours in comparison with high initial ones (by order ~1000MV) up to 200÷300 values. Though later these values are reproducible ones, they aren't accepted as equilibrium ones because according to previous thermodynamic calculations they are less than predictable values in 2÷3 times.

That's why we use the simplified variant of EMF instantaneous fixing [9], i.e. the rapid fixing of EMF values which is earlier applied by us at thermodynamic investigation of ytterbium and neodymium telluride [10,11]. The heart of this method is in the fact that left electrode is in another vessel with the same electrolyte at the same temperature that the right electrodes are up to the moment of EMF measurements. EMF measurement is carried out in the moment of left electrode introduction into electrochemical system with right electrode and the maximum value of EMF is fixed. The measurements are carried out with the help of high-ohmic numerical voltmeter B7-34A in 300÷430K interval.

The measurement results are given in figure and in table. As it is seen EMF temperature dependence is linear one. The obtained experimental data are treated with the help of computer program "Microsoft Office Excel 2003" by the method of least squares. The calculations are given

in table. The linear equation presented in the form recommended in [12] is obtained:

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

n is number of pares of E and T values correspondingly; S_E and S_b are dispersions of separate measurements of EMF and b coefficient; \bar{T} is average absolute temperature, t is Student's test. At confidence level 95% and number of experimental points $n \geq 20$ Student's test $t \leq 2$.

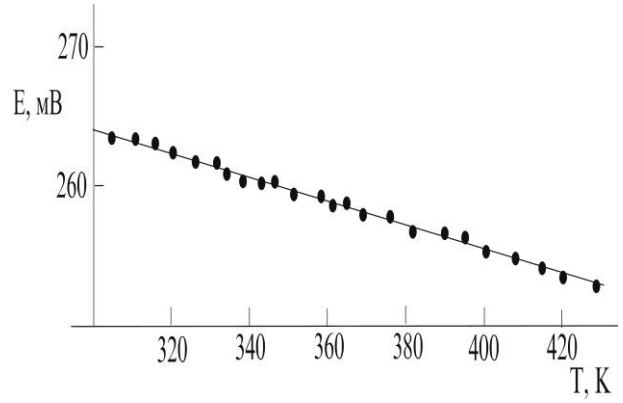


Fig. Temperature dependence of EFM chains of (5.16) type for melts of GdTe-Gd₂Te₃ subsystem.

Table
The results of computer treatment of EFM measurement results for the samples with compositions 51 and 55 at.% of Gd-Te system

T_i, K	E_i, mB	$T_i - \bar{T}$	$E_i(T_i - \bar{T})$	$(T_i - \bar{T})^2$	\tilde{E}	$E_i - \tilde{E}$	$(E_i - \tilde{E})^2$
305,6	964,2	-56,90	-54862,98	3237,61	964,25	-0,05	0,00
311,2	963,8	-51,30	-49442,94	2631,69	963,75	0,05	0,00
316,3	963,4	-46,20	-44509,08	2134,44	963,29	0,11	0,01
321,9	963	-40,60	-39097,80	1648,36	962,79	0,21	0,04
327,2	962,6	-35,30	-33979,78	1246,09	962,32	0,28	0,08
332,3	962,3	-30,20	-29061,46	912,04	961,86	0,44	0,19
334,6	961,8	-27,90	-26834,22	778,41	961,66	0,14	0,02
338,4	961,4	-24,10	-23169,74	580,81	961,32	0,08	0,01
343,9	961	-18,60	-17874,60	345,96	960,83	0,17	0,03
347,7	960,2	-14,80	-14210,96	219,04	960,49	-0,29	0,08
351,2	960,7	-11,30	-10855,91	127,69	960,18	0,52	0,27
358,5	959	-4,00	-3836,00	16,00	959,53	-0,53	0,28
361,9	958,1	-0,60	-574,86	0,36	959,22	-1,12	1,26
365,2	958,5	2,70	2587,95	7,29	958,93	-0,43	0,18
369,1	958,1	6,60	6323,46	43,56	958,58	-0,48	0,23
376,3	957,1	13,80	13207,98	190,44	957,94	-0,84	0,71
381,1	957,2	18,60	17803,92	345,96	957,51	-0,31	0,10
390,7	956,7	28,20	26978,94	795,24	956,66	0,04	0,00
395,8	956,7	33,30	31858,11	1108,89	956,20	0,50	0,25
401,4	956,1	38,90	37192,29	1513,21	955,70	0,40	0,16
408,2	955,9	45,70	43684,63	2088,49	955,10	0,80	0,65
415,2	955,8	52,70	50370,66	2777,29	954,47	1,33	1,77
420,6	955,8	58,10	55531,98	3375,61	953,99	1,81	3,28
425,7	950,7	63,20	60084,24	3994,24	953,53	-2,83	8,03
$\bar{T} =$ 362,5	$\bar{E} =$ 959,17		$\sum E_i(T_i - \bar{T})$ =-2686,17	$\sum (T_i - \bar{T})^2$ =30118,72			$\sum (E_i - \tilde{E})^2$ =17,64

From the obtained equation

$$E, mB = 991,5 - 0,089T \pm 2 \left[\frac{0,80}{24} + 2,6 \cdot 10^{-5} (T - 362,5)^2 \right]^{1/2} \quad (2)$$

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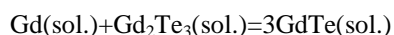
the relative partial thermodynamic functions of Gd in GdTe are calculated by known thermodynamic expressions:

$$\Delta \bar{G}_{Gd} = -279,3 \pm 0,3 \text{ kJ/mol} \quad (3)$$

$$\Delta \bar{H}_{Gd} = -287,3 \pm 1,6 \text{ kJ/mol} \quad (4)$$

$$\Delta \bar{S}_{Gd} = -26,7 \pm 4,3 \text{ J/(mol}\cdot\text{K)} \quad (5)$$

These partial molar values are thermodynamic functions of potential forming reaction [8]:



According to this reaction the standard thermodynamic formation functions GdTe can be calculated by ratios:

$$\Delta_f Z^0(\text{GdTe}) = \frac{1}{3} [\Delta \bar{Z}_{Gd} + \Delta_f Z^0(\text{Gd}_2\text{Te}_3)] \quad (6)$$

(Z≡G,H) and standard entropy by ratio:

$$S^0(\text{GdTe}) = \frac{1}{3} [\Delta \bar{S}_{Gd} + S^0(\text{Gd}) + S^0(\text{Gd}_2\text{Te}_3)] \quad (7)$$

According to these reactions the information by standard thermodynamic formation functions, standard entropy Gd₂Te₃ and also standard entropy of elementary gadolinium.

The standard free Gibb's energy of Gd₂Te₃ formation is calculated and the coherent complex of thermodynamic data for this compound:

$$\Delta_f G^0(298\text{K}) = -930,6 \pm 25,9 \text{ kJ/mol}$$

$$\Delta_f H^0(298\text{K}) = -926,3 \pm 22,2 \text{ kJ/mol}$$

$$S^0(298\text{K}) = 298,9 \pm 8,4 \text{ J/(mol}\cdot\text{K)}$$

is obtained by us with the use of data [8] by standard heat of Gd₂Te₃ formation and also values of standard entropies of gadolinium (67,95±0,84 Дж·моль⁻¹·К⁻¹) and tellurium (49,50±0,21 Дж·моль⁻¹·К⁻¹) [7]. This compound is used at calculations by ratios (6) and (7).

In the result of calculations the following values of standard integral thermodynamic functions of GdTe are obtained:

$$\Delta_f G^0(298\text{K}) = -403,3 \pm 8,7 \text{ kJ/mol}$$

$$\Delta_f H^0(298\text{K}) = -404,4 \pm 7,9 \text{ kJ/mol}$$

$$S^0(298\text{K}) = 113,7 \pm 4,1 \text{ J/(mol}\cdot\text{K)}$$

The errors are found by the method of mistake accumulation.

CONCLUSION

The system is investigated by rapid fixing method in two-phase region of GdTe+Gd₂Te₃ in temperature interval 300-430K. The relative partial molar functions of gadolinium in melts on the base of which the coherent complex of standard thermodynamic function of formation (ΔG_{298}^0 , ΔH_{298}^0) and standard entropy of GdTe compound are firstly obtained.

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