THERMODYNAMIC PROPERTIES OF ERBIUM MONOTELLURIDE

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The results of thermodynamic investigation of ErTe investigation by the method of electromotive force (EMF) are presented in the work. The relative partial molar functions of erbium in ErTe+Er_2Te_3 two-phase region are calculated from data obtained by the method of rapid fixing of EMF. Gibb's standard free formation energy and formation enthalpy and also the standard entropy of ErTe compound are calculated based on obtained data and integral thermodynamic functions of Er_2Te_3.

Keywords: erbium telluride, ErTe, Er_2Te_3, EMF method, thermodynamic functions.
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INTRODUCTION

Rare earth chalcogenides are among the promising materials for electronic equipment. They have a wide range of physical properties: high heat resistance, stability to sudden changes in environmental conditions, unique magnetic, optical and thermoelectric properties [1-10].

For the development of modern preparative methods and controlled synthesis of novel complex phases and materials based on them, the experimental phase diagrams and reliable thermodynamic data are required [11-14].

The Er-Te system [1, 15] is characterized by the formation of tellurides with ErTe, Er_2Te_3, and $ErTe_3$ compositions. ErTe and Er_2Te_3 compounds melt congruently at 1773 and 1486K, while $ErTe_3$ melts with decomposition according to the peritectic reaction at 957 K. ErTe and Er_2Te_3 have a cubic, $ErTe_3$ – rhombic structure.

The thermodynamic properties of erbium telluride are not well understood. In modern reference books [16, 17] no thermodynamic data available on these compounds. In [18], the standard thermodynamic functions of the formation of Er_2Te_3 were determined by direct synthesis from components in a calorimetric bomb. In a later work [19], the authors calculated the standard thermodynamic functions of Er_2Te_3 formation by the EMF method and showed their good agreement with the data [18]. The reference book [20] provides estimated data on the standard enthalpy of formation and entropy of ErTe and Er_2Te_3.

This work presents the results of the study of the thermodynamic properties of monotelluride erbium by the method of electromotive forces (EMF) with glycerol electrolyte. This modification of EMF method was successfully used for the thermodynamic investigations of a number binary and ternary chalcogenide system [21-25].

EXPERIMENT AND THEIR RESULTS

For the investigations of the thermodynamic properties of ErTe compound, the concentration cells of follow type were constructed:

$$(-)\ \mathrm{Er\ (solid)}\ |\mathrm{glycerine + KCl + ErCl_3}\ |\ \mathrm{(Er\text{-}Te)\ (solid)}\ \ (+) \qquad (1)$$

The alloys of Er-Te system with compositions 52 and 57 at Te% (two-phase region ErTe+ Er_2Te_3) were synthesized by ceramic method from elementary high purity erbium and tellurium and used as right electrodes (anode) in cells (1).

The synthesis is carried out in evacuated (10^{-2}Pa) silica tubes ampoules at 1000K. Later the melts are powdered, carefully mixed and pressed in tabs which are annealed at the same temperature during ~800h. The phase compositions are controlled by the XRD method.

The left electrodes (cathod) were prepared by the fixing of metallic erbium on molybdenum wire while the anodes were prepared by pressing of powdered intermediate alloys on the wire in the form of cylinder tabs of mass ~0,5g under pressure of ~0.1 GPa.

As an electrolyte, the KCl glycerin solution with the addition of $ErCl_3$ was used. Because the presence of either moisture or oxygen in the electrolyte was inadmissible, glycerol was thoroughly dewatered and degassed by evacuation at ~450 K over anhydrous chemically pure salts.

During EMF measurements, it was shown the non- equilibrium of cells (1). EMF values strongly decrease in measurement beginning during several hours in comparison with high initial ones (by order ~1000 mV) up to 200÷300 mV. 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. Thus and so we use the simplified variant of EMF instantaneous fixing [26], i.e. the rapid fixing of EMF values which is earlier applied by us at the thermodynamic investigation of some REE tellurides [27-29]. The essence 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.

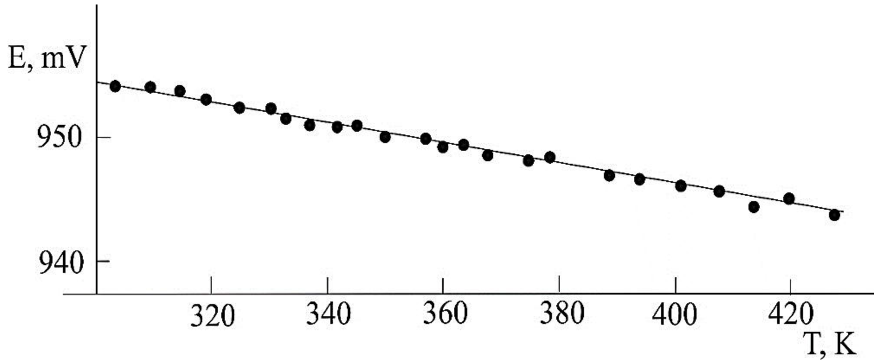

Fig. Temperature dependence of EMF measurements of cell (1) alloys of the ErTe-Er_2Te_3 subsystem

EMF measurement is carried out in the moment of left electrode introduction into the electrochemical system with the right electrode and the maximum value of EMF is fixed. EMF was measured using the high-impedance digital voltmeter B7-34A. Most measurements were performed when heating and cooling the cell in steps up to 10°. Chromel- alumel thermocouple couples and mercury thermometers with an accuracy of about ±0.5° were used to measure the temperature of the electrochemical cell. The chromel- alumel thermocouples were preliminarily calibrated in the temperature interval 300-510 K using elemental Ga, S, In, and Sn as reference materials.

The measurement results are given in Figure and in Table. As can be seen, the temperature dependence of the EMF is almost linear. The obtained experimental data were processed using the "Microsoft Office Excel 2003" computer program using the least-squares method. The steps of the calculations are given in the Table. A linear equation is obtained, presented in the form recommended in [30, 31]

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

Here, *n* -is the number of pairs of *E* and *T* values; S_E and S_b -are the dispersions of separate measurements of EMF and coefficient b, respectively; $\overline{T}$ - average absolute temperature, *t* – is Student's test. At the confidence level of 95% and *n* ≥20, the Student’s coefficient is *k* ≤2.

From the obtained relation

$$E, mV = 979.73 - 0{,}0838T \pm 2\left[\frac{0{,}26}{24} + 8.2\cdot 10^{-6}(T-362{,}84)^2\right]^{1/2} \tag{2}$$

the relative partial thermodynamic functions of Er in ErTe are calculated by known thermodynamic expressions:

$$\Delta\overline{G}_{Er} = -276.36 \pm 0{,}12 \text{ kJ}\cdot\text{mol}^{-1} \tag{3}$$

$$\Delta\overline{H}_{Er} = -283.59\pm{,}0.60 \text{ kJ}\cdot\text{mol}^{-1} \tag{4}$$

$$\Delta\overline{S}_{Er} = -24.25 \pm 0.66 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \tag{5}$$

These partial molar data are thermodynamic functions of potential forming reaction:

$$Er(sol.) + Er_2Te_3 (sol.) = 3Er (sol.)$$

According to this relation the standard thermodynamic formation functions of ErTe were calculated using the relation

$$\Delta_f Z^0(ErTe) = \frac{1}{3}\left[\Delta\overline{Z}_{Er} + \Delta_f Z^0(Er_2Te_3)\right] \tag{6}$$

(Z≡G, H) and standard entropy using relations

$$S^0(ErTe) = \frac{1}{3}\left[\Delta\overline{S}_{Er} + S^0(Er) + S^0(Er_2Te_3)\right] \tag{7}$$

According to these equations, the calculations require information on the standard thermodynamic functions of the formation and standard entropy of Er_2Te_3, as well as the standard entropy of elementary erbium.

We use the data of [19] on the standard heat of formation of Er_2Te_3, as well as the values of the standard entropies of erbium (73.14 ± 0.63 kJ·mol^{-1}) and tellurium (49.50 ± 0.21 kJ·mol^{-1}) [17] the standard Gibbs free energy of the formation of Er_2Te_3 was calculated and a mutually consistent set of thermodynamic data was obtained for this compound:

$$\Delta_f G^0(298K) = -797.4 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^0(298K) = -822.2 \pm 16.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^0(298K) = -83.7 \pm 27.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

These data were used for calculations by relations (6) and (7).

As a result of the calculations, the following values of the standard integral thermodynamic functions of ErTe were obtained:

$$\Delta_f G^0(298K) = -357.0 \pm 0.5 \text{ kJ·mol}^{-1}$$

$$\Delta_f H^0(298K) = -379.6 \pm 6.0 \text{ kJ·mol}^{-1}$$

$$S^0(298K) = 86.7 \pm 9.3 \text{ J·mol}^{-1}\text{·K}^{-1}$$

In all cases, the estimated standard deviations were calculated by the accumulation of errors.

Table.

Experimentally obtained data for temperature and EMF as well as data associated with the calculation steps for the samples with compositions 52 and 57 at.% of Er-Te system

T_i, K	E_i, mV	$T_i - \bar{T}$	$E_i(T_i - \bar{T})$	$(T_i - \bar{T})^2$	$\tilde{E}$	$E_i - \tilde{E}$	$(E_i - \tilde{E})^2$
303,5	954,3	-59,34	-56629,75	3521,43	954,30	0,00	0,00
310,8	953,7	-52,04	-49632,14	2708,34	953,69	0,01	0,00
316,5	953,3	-46,34	-44177,51	2147,55	953,21	0,09	0,01
320,2	953,1	-42,64	-40641,77	1818,31	952,90	0,20	0,04
326,2	952,8	-36,64	-34912,18	1342,61	952,40	0,40	0,16
333,4	952,1	-29,44	-28031,41	866,81	951,80	0,30	0,09
334,3	951,8	-28,54	-27165,96	814,63	951,72	0,08	0,01
338,5	951,3	-24,34	-23156,23	592,52	951,37	-0,07	0,00
343,2	951,7	-19,64	-18692,97	385,80	950,97	0,73	0,53
347,6	950,6	-15,24	-14488,73	232,31	950,61	-0,01	0,00
353,3	950,8	-9,54	-9072,22	91,04	950,13	0,67	0,45
358,5	949,4	-4,34	-4121,98	18,85	949,69	-0,29	0,09
362,7	948,1	-0,14	-134,31	0,02	949,34	-1,24	1,54
365,2	948,6	2,36	2237,11	5,56	949,13	-0,53	0,28
369,4	948,2	6,56	6218,61	43,01	948,78	-0,58	0,34
376,5	947,3	13,66	12938,54	186,55	948,18	-0,88	0,78
381,1	947,5	18,26	17299,77	333,37	947,80	-0,30	0,09
390,6	946,7	27,76	26278,81	770,53	947,00	-0,30	0,09
395,3	946,8	32,46	30731,55	1053,54	946,61	0,19	0,04
401,8	946,1	38,96	36858,48	1517,75	946,07	0,03	0,00
408,3	946	45,46	43003,58	2066,46	945,52	0,48	0,23
417,2	945,8	54,36	51412,11	2954,83	944,77	1,03	1,05
424,6	943,7	61,76	58281,34	3814,09	944,15	-0,45	0,21
429,5	944,2	66,66	62938,80	4443,33	943,74	0,46	0,21
$\bar{T}$ =362,84	$\bar{E}$ =949,3292		$\sum E(T_i - \bar{T})$ =-2658,45	$\sum (T_i - \bar{T})^2$ = 31729,24			$\sum (E_i - \tilde{E})^2$ = 6,23

CONCLUSION

The fast fixation method was used to study the Er-Te system in the two-phase region ErTe Er_2Te_3 in the temperature range 300-430 K. Relative partial molar functions of erbium in alloys were calculated, based on which a mutually consistent complex of standard thermodynamic formation functions and standard entropy of the ErTe compound was obtained for the first time.

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