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【論 文】

Standard Enthalpies of Formation for Some Phases in the YBaCuO System

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On the basis of statistical treatment and empirical dependencies of literature data the standard enthalpies of formation from simple oxides, $\Delta_f H^\circ_{ox}$ (298), have been estimated for $YBa_2Cu_3O_6$, $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.5}$, $YBa_2Cu_3O_7$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$, $YBa_4Cu_3O_{8.5}$, Y_2BaCuO_5, $Y_2Cu_2O_5$, $YCuO_2$, Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$ and $Y_4Ba_3O_9$.

1. Introduction

For every compound a standard enthalpy of formation is one of the most important thermochemical characteristics. The determination of these quantities of the YBaCuO system has not been finished yet: for some phases those data are doubtful enough, for other phases are unknown.

In **Table 1** the standard enthalpies of formation from simple oxides, $\Delta_f H^\circ_{ox}$(298), (further abreviated **SEF**[+]), are given for 12 complex oxides according to Refs.1-43. As it is seen from **Table 1**, various experimental and calculation methods were used for determining SEF. But the results for the same compounds by different researchers do not agree in spite of similar investigation methods. The considerable difference with each other of the SEF values does not permit to account the data reported by individual investigators to be reliable enough, as well as those by various groups. Therefore it is reasonable to use some statistical methods for deriving the more reliable values.

In the present work for 12 complex oxides the series of average arithmetic values were derived as the basic SEF from the data of **Table 1**. The basic SEF's were used for the construction of the empirical dependencies of SEF on the number of oxygen atoms in a molecular unit of the compound, (m_0), or on the number of atoms in the unit cell (ΣN), or a molecular masses of the unit cell of a compounds (ΣM). It was completed by evaluation dependencies related to ln (ΣN) and ln (ΣM). With the help of these empirical equations the SEF's for $YBa_2Cu_3O_6$, $YBa_2Cu_3O_{6.5}$, $YBa_2Cu_3O_7$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$, $YBa_4Cu_3O_{8.5}$, Y_2BaCu_5, $YCuO_2$, $BaCuO_2$, $BaCu_2O_2$, Ba_2CuO_3, Ba_3CuO_4, $Ba_2Cu_3O_5$, $Ba_3Cu_5O_8$, Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, and $Y_4Ba_3O_9$, have been calculated.

The results were compared with the date reported by us earlier[3, 20] and with some more recent values.

+) $\Delta_f H^\circ_{ox}$, the standard enthalpy of formation from the relevant simple oxides, is the enthalpy change accompanying the formation of one mole of a complex oxide $A_x B_y C_z O_n$ from component simple oxides $A_x O_{n_1}$, $B_y O_{n_2}$ and $C_z O_{n_3}$ (where $n = n_1 + n_2 + n_3$) at the standard temperature of 298.15K.

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Table 1(a) Review of standard enthalpies of formation for complex oxides in the YBaCuO system.

N	$\Delta H^{\circ}_{ox}(298)$	$\Delta H^{\circ}_{ox}(T)$	Reference	Notes
	$YBa_2Cu_3O_x$, $x \cong 7$			
1	−126.0	–	[1]	x = 6.98, calorimetry of solution.
2	−126.0	–	[2]	x = 7.0, calculation based on phase structural somponents.
3	−204.9	–	[3]	x = 7.0, calculation the basis of empirical dependencies.
4	−202.0	–	[4]	x = 7.0, the same.
5	−133.0	–	[5]	x = 7.0, calculation the based on energetic of phase structural components.
6	−127.0	–	[6]	x = 7.0, the some.
7	−146.0	–	[7]	x = 7.0, calorimetry of solution.
8	−142.0	–	[8]	x = 7.0, calculation the based on energetic of phase structural components (with BaO_2).
9	−152.0 −146.3	–	[9]	x = 7.0, calculation by models of regular and ideal solution 123-O_7 and 123-O_6.
10	−123.0	–	[10]	x = 6.93, calculation by model 123-O_y, offered by S.A.Degtyrev.
11	−122.5	–	[11]	x = 6.9, calorimetry of solution.
12	−125.0	–	[12]	x = 7.0, extrapolated from 19 experimental points between y = 6.2 and y = 6.93.
13	−106.2 −116.6	–	[13]	x = 6.92 and 6.88, calorimetry of solution.
14	−116.8	–	[14]	x = 6.98, the same.
15	−132 ± 20	–	[15]	x = 6.96, the same.
16	−110 ± 10	–	[16]	x = 6.92, the same.
17	−154.6 −231.9	–	[17]	x = 7.0, the same.
18	−70.1*	−66.6 ± 20	[18]	x = 7.0; 800-900 ℃, EMF
19	−80.4*	−75 ± 22	[18]	x = 6.7; 650 ℃, calorimetry of solution.
	$YBa_2Cu_3O_x$, $x \cong 6$			
1	−50.0	–	[1]	x = 6.25, calorimetry of solution.
2	−175.6	–	[3]	x = 6.0, calculation the basis of empirical dependencies.
3	−165.8	–	[5]	x = 6.0, calculation the based on energetic of phase structural components.
4	−219.4 −181.4	–	[9]	x = 6.0, calculation by models of regular and ideal solution 123-O_7 and 123-O_6.
5	−84	–	[10]	x = 6.2, calculation by model 123-O_y, offered by S.A.Degtyrev.
6	−62	–	[10]	x = 6.2, the same.
7	−37.5	–	[11]	x = 6.2, extrapolated from 19 experimental points between y = 6.2 and y = 6.93.
8	−94.1	–	[13]	x = 6.09, calorimetry of solution.
9	−72.4	–	[13]	x = 6.3, the same.
	$YBa_2Cu_3O_8$			
1	−228.3 ± 25.9	–	[7]	Calorimetry of solution.
2	−155.8 ± 6.7	–	[13]	The same.
3	−234.2	–	[20]	Calculation the basis of empiric dependencies. Error taken into account sfter publication or the work.
4	−156 ± 25	–	[15]	Calorimetry of solution.
5	−146 ± 10	–	[16]	The same.
6	−121.5	−105 ± 18	[19]	650 ℃, calorimetry of solution.
	Y_2BaO_4			
1	−117.1	–	[20]	Calculation the basis of empiric dependencies.
2	−33.9 ± 2.8	–	[21]	Calorimetry of solution.
3	+18.47	–	[22]	Experiment.
4	−120.0*	−120.1	[23]	717-1021 ℃, EMF.
5	−85.0*	−85 ± 12	[19]	650 ℃, calorimetry of solution.
6	−36 ± 3	–	[24]	Calorimetry of solution.
7	−46 ± 11	–	[25]	Pressure of vapor.

Table 1(b) Review of standard enthalpies of formation for complex oxides in the YBaCuO system.

N	$\Delta H^{\circ}_{ox}(298)$	$\Delta H^{\circ}_{ox}(T)$	Reference	Notes
		$Y_4Ba_3O_9$		
1	−263.5	−	[20]	Calculation the basis of empiric dependencies.
2	−317.0*	−317.5	[22]	575-975℃, EMF.
3	+22.6*	23.5	[19]	650℃, calorimetry of solution.
4	−115±25	−	[25]	Pressure of vapor.
		Ba_2CuO_3		
1	−87.8	−	[20]	Calculation the basis of empiric dependencies.
2	−129±15*	−129±15	[19]	650℃, calorimetry of solution.
		$BaCuO_2$		
1	−58.5	−	[20]	Calculation the basis of empiric dependencies.
2	−86	−	[26]	Calorimetry of solution.
3	−93.3±6	−	[27]	The same.
4	−49.6	−	[28]	Estimation.
5	−98.1	−	[17]	Calorimetry of solution.
6	−117.8	−	[7]	The same.
7	−53.2	−	[21]	The same.
8	−66±5	−	[11]	The same.
9	−85.2±2.4	−	[13]	The same.
10	−43.9	−	[29]	The same.
11	−63.4	−	[30]	The same.
12	−98.5±7.9	−	[15]	The same.
13	−83.8±3.1	−	[16]	The same.
14	−52.9*	−53.8±12	[18]	800-900℃, EMF.
15	−43.1*	−43.9	[31]	950-1200℃, EMF.
16	−56.4*	−57±12	[19]	650℃, calorimetry of solution.
		Y_2BaCuO_5		
1	−92.0	−	[26]	Calorimetry of solution.
2	+83.4	−	[28]	Estimation.
3	−78.3	−	[17]	Calorimetry of solution.
4	−76.2±22	−	[7]	The same.
5	−131.9	−	[20]	Calculation the basis of empiric dependencies.
6	−83±25	−	[11]	Calorimetry of solution.
7	−48.6±3	−	[13]	The same.
8	−24.4	−	[29]	The same.
9	−72.5	−	[8]	Calculation the based on energetics of phase structural somponents.
10	−152.5	−	[27]	Calorimetry of solution.
11	−61.15	−	[32]	The same.
12	−57.6±7.9	−	[15]	The same.
13	−52.9±3	−	[16]	The same.
14	−56.4*	−59.3±3	[16]	702℃, calorimetry of solution.
15	−149.2*	−152.5	[23]	717-1021℃, EMF.
16	−45.2*	−48.4±11.9	[18]	800-900℃, EMF.
17	−53.3*	−56±18	[19]	650℃, calorimetry of solution.
18	−64.0	−	[41]	Calculation the based on energetics of phase structural somponents.
		$Y_2Cu_2O_5$		
1	−56	−	[17]	Calorimetry of solution
2	−9.2±3.2	−	[16]	The same.
3	−12.2±2.7	−	[13]	The same.
4	15.9	−	[28]	Estimation.
5	−54.0	−	[21]	Calorimetry of solution
6	−15±12	−	[11]	The same.
7	−72.3**	−	[33]	923-1223 K, EMF.
8	−50.3**	−	[34]	EMF.
9	14.3	−	[29]	Calorimetry of solution
10	26.8*	20.7±2.5	[35]	900-1075℃, EMF.
11	15.6*	11.2	[36]	600-1050℃, EMF.
12	21.3*	18.5	[37]	590-700℃, EMF.
13	−15.4*	−19.45	[38]	675-925℃, EMF.
14	11.4*	2.8±1.7	[18]	1050-1300℃, EMF.
15	14.0*	9.1	[39]	900-1075℃, EMF.
16	15.8*	10.9	[23]	717-1021℃, EMF.
17	9.85*	−6.6±2.9	[16]	702℃, calorimetry of solution.
18	7.7*	−4.8±8	[19]	650℃, calorimetry of solution.
		$YBa_4Cu_3O_{8.5}$		
1	−233.1*	−238±25	[19]	650℃, calorimetry of solution.
2	−248.8	−	[20]	Calculation the basis of empiric dependencies.
		$YCuO_2$		
1	−58.6	−	[20]	The same.
2	−26.9	−	[36]	EMF.
3	−4.3	−	[40]	Caluculated value.
		$BaCu_2O_2$		
1	−59.5	−	[20]	Calculation the basis of empiric dependencies.
2	−46.5*	−46.5±3.9	[42]	1000-1100 K, EMF.
3	−8.74*	−8.74	[43]	1000 K. EMF.
4	+25.2	−	[43]	Calorimetry

2. Analysis of $\Delta_f H^\circ_{ox}$ (298) values

2.1 The definition of basic and probable SEF

We have taken the average arithmetic values as the basic SEF's for $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, $YBa_2Cu_4O_8$, Y_2BaCuO_5, $Y_2Cu_2O_5$, $BaCuO_2$, $BaCu_2O_2$, Ba_2CuO_3, and Y_2BaO_4 and calculated the quadratic deviations.

By this operation we have excluded the data in ref [3, 4] and [18, 19] for $YBa_2Cu_3O_7$ as a casual (the maximum and minimum values of SEF). On the same ground the data [91] and [11] have been excluded for $YBa_2Cu_3O_6$. We have not used the data from Ref [22] for Y_2BaO_4 as the sign of the SEF differs from those date reported by the majority of investigators. By the same reasons the data for $Y_2Cu_2O_5$ have been excluded from analysis. The data Ref [28] for Y_2BaCuO_5 and the data of [17, 21, 33, 34, 38] for $Y_2Cu_2O_5$ and the data [43] for $BaCu_2O_2$ obtained by calorimetry.

As follows the results of various investigators differs from each other very considerably for $YCuO_2$, $Y_4Ba_3O_9$, and $YBa_4Cu_3O_{8.5}$. Besides, their number is no satisfactory for the appropriate definition of the average arithmetic basic values. Therefore we can definite three average arithmetic SEF's of the phases as a most probable value. The results 1f definition are given in **Table 2** (column 3).

Table 2 Derived standard enthalpies of formation for complex oxides in the YBaCuO system.

N	Compound	$\Delta_f H^\circ_{ox}$(298) in kJ mol^{-1}			$\Delta_f H^\circ_{el}$(298
		Basic values values and probable values*	Values, received in work	Values, calucurated by Eq.(1)	in kJ mol^{-1} according to this work
1	$BaCuO_2$	−73.4 ± 21.4	−73.4 ± 21.4	−59.5	−781.8
2	Ba_2CuO_3	−108 ± 29	−108 + 29	−89.2	−1370.1
3	Y_2BaO_4	−73 ± 40	−61.2 ± 0.7	−119.0	−2533.5
4	Y_4Ba_3O	−224.3 ± 145	−183.8 ± 9.3	−267.7	−5683.4
5	Y_2BaCuO_5	−76.4 ± 36.4	−84.6 ± 2.6	−148.7	−2712.0
6	$YBa_2Cu_3O_6$	−110.7 + 54.5	−126.6 ± 7.9	−178.4	−2586.8
7	$YBa_2Cu_3O_7$	−129.7 ± 14.3	−134.2 ± 2.4	−208.2	−2706.3
8	$YBa_2Cu_4O_8$	−173.6 ± 46.4	−154 ± 5.7	237.9	−2881.2
9	$YBa_4Cu_3O_{8.5}$	−241 ± 11.2*	−190.2 ± 14.2	252.8	−3828.3
10	$Y_2Cu_2O_5$	+14.5 ± 5.1	−14.5 ± 5.1	−148.7	−2214.8
11	$YCuO_2$	−11.3 ± 15.6*	−4.5 ± 24.3	−59.5	−1038.6
12	$BaCu_2O_2$	−38.2 ± 26.6	−30.1 ± 12.4	59.5	−750.8
13	$Ba_2Cu_3O_{6.5}$	−	−130.8 ± 3.3	−193.3	−2662.5
14	$YBa_2Cu_{3.5}O_{7.5}$	−	−144.6 ± 3.5	−223.0	−2594.5
15	$YBa_2Cu_5O_9$	−	−172.7 ± 10.5	−267.7	−3055.2
16	Ba_3CuO_4	−	−138.7 ± 6.4	−119.0	−1953.7
17	$Ba_3Cu_5O_8$	−	−210.9 ± 4.9	−237.9	−2646.5
18	$Ba_2Cu_3O_5$	−	−147.7 ± 18.5	−148.7	−1719.4
19	$Y_2Ba_2O_5$	−	−97.6 ± 6.4	−148.7	−3123.2
20	$Y_2Ba_4O_7$	−	−169.1 ± 7.5	−208.2	−4301.2

2.2 Evaluation of empirical dependencies calculation of $\Delta_f H^\circ_{ox}$ (298) values

On the basis of analyzing the data of **Table 2** his found, that it is possible to divide all the basic SEF's into three groups:

(1) The phase $Y_2Cu_2O_5$, which is metastable at 298 K ($\Delta_f H^\circ_{ox}$ (298) $= +14.5 ^{+}_{-} 5.1$ kJ mol^{-1});

(2) The rest of the Y-containing oxides and $BaCu_2O_2$;

(3) The oxides in the Ba-C-O system ($BaCuO_2$ & Ba_2CuO_3),

In the **Fig.1** for the second group of the compounds the dependencies of SEF on m_0, ΣN, ln ΣN, ΣM and ln ΣM

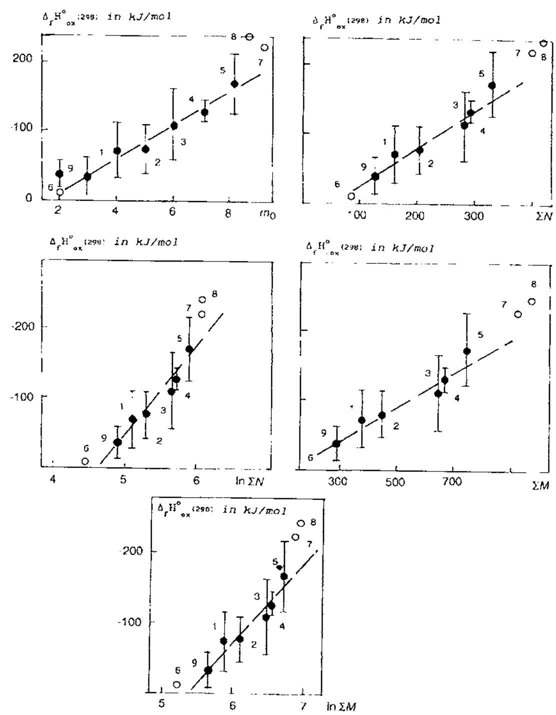

Fig.1 The dependencies of SEF on m_0, ΣN, ln ΣN, ΣM and ln ΣM for the basic SEF of complex oxides in the YBaCuO system.
1- Y_2BaO_4, 2- Y_2BaCuO_5, 3- $YBa_2Cu_3O_6$, 4- $YBa_2Cu_3O_7$, 5- $YBa_2Cu_4O_8$, 6- $YCuO_2$, 7- $Y_4Ba_3O_9$, 8- $YBa_4Cu_3O_{8.5}$ and 9- $BaCu_2O_2$
●- basic value, ○- probable value.

Table 3 The set of emperical Equations for calculation of $\Delta_f H^\circ_{ox}(298)$ in the YBaCuO system (kJ mol^{-1}).

For Y-containing compounds (except $Y_2Cu_2O_5$) and $BaCu_2O_2$ $\Delta_f H^\circ_{ox}(298)^* =$	For compounds in the BaCuO system $\Delta_f H^\circ_{ox}(298)^* =$
$40.02 - 25.45\ m_0$;	$-3.40 - 35\ m_0$;
$31.75 - 0.56\ \Sigma N$;	$-18.166 - 0.547\ \Sigma N$;
$603.72 - 129.94\ \ln \Sigma N$;	$255.57 - 71.283\ \ln \Sigma N$;
$32.86 - 0.25\ \Sigma M$;	$-20.25 - 0.228\ \Sigma M$;
$718.76 - 131.32\ \ln \Sigma M$;	$303.58 - 69.17\ \ln \Sigma M$;

* $- m_0$ is number of oxygen atoms in a molecule of the compound;
ΣN is sum of numbers of elements in the unit cell
ΣM is molecular mass of the compound.

are presented. As it is seen from **Fig.1**, his possible to establish the linear dependences. $\Delta H^\circ_{ox}(298)$ upon those characteristic quantities of oxides with in the limits of their quadratic deviations of the basic SEF values. These dependencies are listed in **Table 3**.

In the Ba-Cu-O system only two basic SEF values for $BaCuO_2$ and Ba_2CuO_3 were known. We made as up position that in this system the similar dependencies of the SEF's on m_0, ΣN, $\ln \Sigma N$, ΣM and $\ln \Sigma M$ also exist, and we constructed these dependencies (**Table 3**).

We calculated the SEF for every compound, except $Y_2Cu_2O_5$, by using the five corresponding equations from **Table 3**. Then we derived the average arithmetic SEF values and quadratic deviations.

3. Results and Discussion

The SEF calculated with the help of above mentioned methods are presented in **Table 2** (column 14). Their values are consistent with the basic SEF within the limits their quadratic deviations. This fact gives us a base to account that the use a set of the empirical dependencies is correct enough to derive the probable values of $\Delta_f H^\circ_{ox}(298)$ for $YCuO_2$, $Y_4Ba_3O_9$ and $YBa_4Cu_3O_{8.5}$. The equations can be similarly employed for the estimation of unknown SEF's of other complex oxides.

For $Y_2Cu_2O_5$ we have taken an average arithmetic value of SEF, equal to $+14.5 \pm 5.1$ kJ mol^{-1}, as the most reliable.

It should be noted, that in the Ba-Cu-O system the calculation of desired SEF for Ba_3CuO_4, $Ba_3Cu_5O_8$ and $Ba_2Cu_3O_5$ were made on the ground of only two basic SEF's, and those as received data must be confirmed and possibly revised in future.

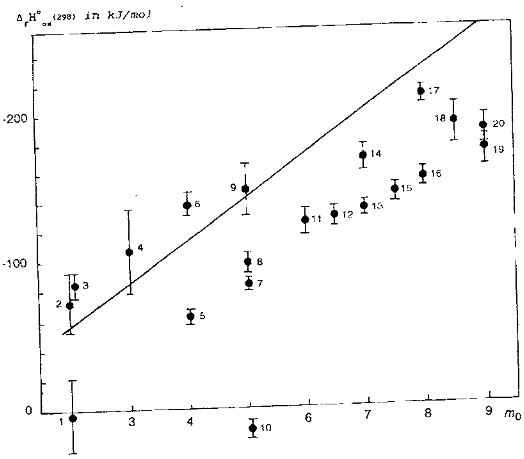

Fig.2 The dependencies of $\Delta_f H^\circ_{ox}$ (298) for complex oxides in the YBaCuO system on number of oxygen atoms in a molecule of oxide according to this work:
1- $YCuO_2$, 2- $BaCuO_2$, 3- $BaCu_2O_2$,
4- Ba_2CuO_3, 5- Y_2BaO_4, 6- Ba_3CuO_4,
7- Y_2BaCuO_5, 8- $Y_2Ba_2O_5$, 9- $Ba_2Cu_3O_5$,
10- $Y_2Cu_2O_5$, 11- $YBa_2Cu_3O_6$, 12- $YBa_2Cu_3O_{6.5}$
13- $YBa_2Cu_3O_7$, 14- $Y_2Ba_4O_7$, 15- $YBa_2Cu_{3.5}O_{7.5}$
16- $YBa_2Cu_4O_8$, 17- $Ba_3Cu_5O_8$,
18- $YBa_4Cu_3O_{8.5}$, 19- $YBa_2Cu_5O_9$, 20- $Y_4Ba_3O_9$
and the line according to Eq.(1).[3,20]

In the previous papers [3, 20] we supposed for the estimation of $\Delta_f H^\circ_{ox}(298)$ the empirical equation.

$$\Delta_f H^\circ_{ox}(298)(i) = -29.274\, m_0,\ \text{kJ mol}^{-1} \quad (1)$$

It is interesting to compare the data of present work with the results of calculation by Eq.(1). (See **Table 2**, column 5 and **Fig.2**). It is shown in **Table 2** and **Fig.2**, that the of SEF deviates negatively from the calculated values with in creasing m0. But for the majority of the complex oxides the values of $\Delta H^\circ_{ox}(298)$ calculated by Eq.(1) are more negative than the data calculated in present work.

The values of standard enthalpy of formation from $\Delta_f H^\circ_{ox}(298)$, are given in **Table 2** (column 6). We do not have any oppurtunities to include all published data in our work. Therefore it is interesting to compare some

Table 4 Comparison between $\Delta_f H^\circ_{ox}(298)$ of some complex oxides in the YBaCuO system derived in this work with literature data.

Oxide	$\Delta_f H^\circ_{ox}(298)$ in kJ mol^{-1} this work	Literature data	δ in %	Note to literature data
$YBa_2Cu_3O_{6.5}$	−130.8	+19.8 [43]	+115.1	1000 K EMF.
	−130.8	−9.8 [43]	+92.5	Calorimetry
Y_2BaCuO_5	−84.6	+2.7 [43]	+103.2	1000 K EMF.
	−84.6	+6.6 [43]	+107.8	Calorimetry
$Y_2Cu_2O_5$	+14.5	+31.5 [43]	+117.2	1000 K EMF.
	+14.5	+26.5 [43]	+82.8	Calorimetry
$BaCuO_2$	−73.4	−0.5 [43]	+99.3	1000 K EMF.
	−73.4	−69.0 [43]	+6.0	$BaCuO_{2.04}$, Calorimetry
$BaCu_2O_2$	−30.1	−8.7 [43]	+71.1	1000 K EMF.
	−30.1	+25.2 [43]	+183.7	Calorimetry
$Y_2Ba_4O_7$	−169.1	−199.3 [43]	−17.9	1000 K EMF.
	169.1	−241.7 [43]	−42.9	Calorimetry
$BaCuO_2$	−73.4	−82.0 [48]	−11.7	$BaCuO_2$, Calorimetry
$BaCuO_2$	−73.4	−66.0 [49]	+10.1	Calorimetry
$YBa_2Cu_3O_{6.5}$	−130.8	−79.0 [49]	+39.6	Calorimetry
$YBa_2Cu_3O_7$	−134.2	−122.0 [49]	+9.1	$YBa_2Cu_3O_{6.9}$, Calorimetry
$YBa_2Cu_3O_7$	−134.2	162 [50]	+53.8	$YBa_2Cu_3O_{6.965}$, Calorimetry
$YBa_2Cu_3O_{6.5}$	−130.8	−96±15 [51]	+26.6	*
$YBa_2Cu_4O_8$	−154.0	−143.3 [52]	+6.9	*

* — calculated on the basis of theoretical analysis.

recently published values with our results (**Table 4**). As seen in Table 4, the recent data [48-52] provided by precise experiments [48-50] as well as theoretical analysis determined by [51-52] are in agreement with our data. The results of experimental investigations [43] and [53] differs very considerably from our data as well as from the data of other investigators (see **Tables** 1 & 4) with exception of the SEF for $Y_2Ba_4O_7$ and $BaCuO_2$ (calorimetry).

The possible reason for these differenceis can be a systematic error in the investigation methods, as for the majority of the data [43, 53] the sign of deviations is constant (and positive).

4. Conclusion

With application of a statistical treatment to literature data of 12 complex oxides in the YBaCuO system the empirical dependencies of $\Delta_f H^\circ_{ox}(298)$ values have been revised and estimated for 20 complex oxides supposed to exist in the above treated YBaCuO system.

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