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Final account of the thermochemical properties of complex oxides in the Y–Ba–Cu–O system ☆

N. Ilynych[a], S. Zaitzeva[a], G. Moiseev[a], J. Šesták[b,*], N. Vatolin[a]

[a] *Institute of Metallurgy, Ural Division of Russian Academy of Sciences, 101, Amundsen Str.,*
Ekaterinburg, 620219, Russian Federation
[a] *Institute of Physics of Academy of Sciences of the Czech Republic, 10, Cukrovarnicka Str.,*
162 00, Prague, Czech Republic

Abstract

The thermochemical properties (ΔH^0_{298}, S^0_{298}, H^0_{298}–H^0_0, $C_p(T)$, T and ΔH phase transformation) for $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$, $YBa_4Cu_3O_{8.5}$, Y_2BaCuO_5, $YCuO_2$, $Y_2Cu_2O_5$, Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, $Y_4Ba_3O_9$, $BaCuO_2$, $BaCu_2O_2$, Ba_2CuO_3 and $Ba_3Cu_5O_8$ are presented. For every complex oxide, the numerical coefficient of the polynomial approximation of the reduced Gibbs energy temperature dependence is calculated.

Keywords: Oxide; Superconductor; Thermodynamic data

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1. Introduction

The thermochemical properties of the ceramic superconductors $YBa_2Cu_3O_7$ (123-O_7), $YBa_2Cu_{3.5}O_{7.5}$ (123.5-$O_{7.5}$), $YBa_2Cu_4O_8$ (124-O_8) and also other phases in the Y–Ba–Cu–O system are being investigated very actively, but this work is not yet finished. Reviews of the known and available thermochemical properties such as ($H^0_{298}-H^0_0$ and the phase transformation temperatures [1], standard entropies of formation [2], heat capacities in crystalline state [3], heats of melting/decomposition [4], average heat capacities of phase transformation products [5] and standard

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[*] Corresponding author.

☆ Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

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enthalpies of formation [6]) are available. On the basis of this information and with the help of different calculation [6, 7] and statistical methods, we present here the most reliable data.

In this article the results of previous investigations are summarized. In addition to the above mentioned superconductors, data are also given for $YBa_2Cu_3O_6$ (123-O_6), $YBa_4Cu_3O_{8.5}$ (143-$O_{8.5}$), Y_2BaCuO_5 (211-O_5), $YCuO_2$, $Y_2Cu_2O_5$, Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, $Y_4Ba_3O_9$, $BaCuO_2$, $BaCu_2O_2$, Ba_2CuO_3 and $Ba_3Cu_5O_8$. For double oxides in the Y_2O_3–BaO and BaO–CuO systems, the correction of standard enthalpies of formation [6] was carried out with the use of semiempirical regularities [8].

For every complex oxide in the interval from 298 to 6000 K, the numerical coefficients of the polynomials and the approximate reduced Gibbs energy temperature dependence were calculated with the help of the pocket program ASTRA [9].

2. Investigation methods and results

The multitude of literature data on the properties of complex oxides, their critical analysis and calculation, and also the statistical methods used for determining reliable data, were described in details elsewhere [1–6].

The standard enthalpies of double oxides in the Y_2O_3–BaO and BaO–CuO systems [6] have been corrected with the help of a linear approximation rule (LAR) [8]. The essence of this empirical regularity is as follows. After studying the 34 quasi-binary AO–BO systems, we found [8] that for the relative double compounds $A_xB_yO_z$, linear dependences between the standard enthalpy of formation from the simple oxides AO and BO ($H^0_{at}(f)j$ in kJ per g-atom) and of those of composition corresponding to the sum of the mole fraction of the standard enthalpies AO and BO ($\bar{H}^0_{at}(j)$ in kJ per g-atom), and also between standard enthalpies AO and BO (H^0_{at}(AO) and H^0_{at}(BO) in kJ per g-atom) are observed. In common the dependence

$$H^0_{at}(f)j = f\,[H^0_{at}(\mathrm{AO}),\ \bar{H}^0_{at}(j),\ H^0_{at}(\mathrm{BO})]\ \text{(kJ per g-atom)} \qquad (1)$$

exhibits a minimum (H^0_{at}(f)min). Its branches can be described with help of linear equations between H^0_{at}(AO) and H^0_{at}(f)min, and H^0_{at}(f)min and H^0_{at}(BO) with the mean deviations from the reference data below ± 5%. This empirical regularity we named the linear approximation rule (LAR) [8].

The initial data were taken from Ref. [6] and the results of the correction according to the LAR for double oxides in the Y_2O_3–BaO and BaO–CuO systems are presented in Table 1 together with the linear equations (1) and necessary explanations. Fig. 1 illustrates the application of LAR graphically. The final thermochemical properties of the complex oxides are given in Table 2.

3. Discussion

The properties of the main phases in the Y–Ba–Cu–O system have been determined under the assumption that every complex oxide has a definite stoichiometric composi-

Table 1
The initial data and results of correction of ΔH^0_{298}(ox) values [6] for double oxides in the Y_2O_3–BaO and BaO–CuO systems using the linear approximation rule [8]

No.	Oxide	$\bar{H}^0_{at}$/kJ per g-atom [a]	H^0_{at}(f)/kJ per g-atom [b]		δ/%	ΔH^0_{298}(ox)/kJ mol^{-1}	
			According to Ref. [6]	According to LAR		According to Ref. [6]	According to LAR
			Y_2O_3–BaO				
1.	Y_2O_3	−383.88 [c]	0	0 [d]	0	0	0
2.	Y_2BaO_4	−329.85	−8.743±0.1	−8.743	0	−61.2	−61.2
3.	$Y_4Ba_3O_9$	−319.20	−11.550±0.6	−10.500	+9.1	−184.8	−168.0
4.	$Y_2Ba_2O_5$	−311.80	−10.844±0.7	−11.710	−8.0	−97.6	−105.5
5.	$Y_2Ba_4O_7$	−297.92	−13.080±0.6	−14.000	−7.0	−169.1	−182.0
6.	BaO	−276.64	0	0	0	0	0
					$\delta = \pm 4.8$		
			BaO–CuO				
1.	BaO	−276.64	0	0 [e]	0	0	0
2.	$BaCuO_2$	−177.11	−18.35±5.35	−18.40	−0.3	−73.4	−73.6
3.	Ba_2CuO_3	−210.08	−18.0±4.83	−24.50	−36.1	−108.0	−147.0
4.	$Ba_3Cu_5O_8$	−152.22	−13.20±0.31	13.80	−4.5	−210.9	−220.8
5.	Ba_3CuO_4	−226.87	−17.34±0.80	−18.32	−5.6	−138.7	−146.6
6.	$Ba_2Cu_3O_5$	−157.20	−14.77±1.85	−14.72	+0.3	−147.7	−147.2
7.	CuO	−77.58	0	0	0	0	0
					$\delta = \pm 6.7$		

Using the example of Y_2BaO_4:

[a] $H^0_{at} = x(Y_2O_3)[\Delta H^0_{298}(Y_2O_3)]/5 + x(BaO)[\Delta H^0_{298}(BaO)]/2 = 0.5(-1919.4/5) + 0.5(-553.5/2) = -329.85$ kJ g-atom, where $x(i)$ is the molar fraction of the ith simple oxide in complex one.

[b] $H^0_{at}(f) = \Delta H^0_{298}(ox)/m = (-61.2 \pm 0.7)/7 = 8.743 \pm 0.1$ kJ g-atom, where m is number of atoms in a molecule of Y_2BaO_4.

[c] Previously used, 1905.4 [10], currently used, 1919.4 kJ mol^{-1}.

[d] The calculation: $H^0_{at}(f) = -62.941 - 0.1643\bar{H}^0_{at}(j)$, for points 1–5, in kJ per g-atom.

[e] The calculations: $H^0_{at}(f) = -101.828 - 0.3681\ \bar{H}^0_{at}(j)$, for points 1,3,5, in kJ per g-atom, and $H^0_{at}(f) = 14.3435 + 0.1849\ \bar{H}^0_{at}(j)$, for points 2–4,6,7, in kJ g-atom.

tion which does not change up to the phase transformation temperature. But the results of investigations [12–15] show that the majority of complex oxides in this system change their oxygen content with increasing temperature. This can be accompanied by changes in the initial composition and formation of new phases and solutions. Accounting for this fact and also for the accuracy of the determination methods [1–6], we can consider that data for $H^0_{298} - H^0_0$ [1], S^0_{298} [2] and also $C_p(T)$ [3] should be reliable enough up to a temperature approximately equal to 0.8 T (ph.tr.). At higher temperatures it is possible to account for the change in the initial compositions of some phases and, consequently, for the changes in the temperature heat capacity equations.

According to Ref. [1], phase transformation temperatures (decomposition in the crystalline state, congruent melting) were found by varying oxygen partial pressure and partly under non-equilibrium conditions. Therefore, the phase transformation tem-

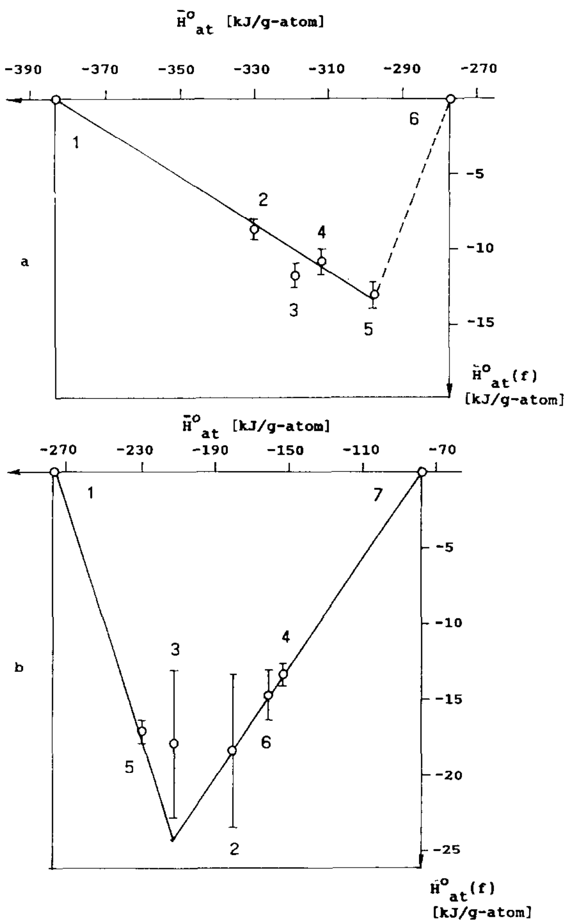

Fig. 1. The dependences of the standard enthalpies of formation from simple oxides of the relative double compounds, $H^0_{at}(f)$ (kJ per g-atom), from the sum of the partial molar enthalpies of the constituent simple oxides (H^0_{at} in kJ per g-atom) for double oxides in the Y_2O_3–BaO (a) and BaO–CuO (b) systems.

(a) 1, Y_2O_3; 2, Y_2BaO_4; 3, $Y_4Ba_3O_9$; 4, $Y_2Ba_2O_5$; 5, $Y_2Ba_4O_7$; and 6, BaO. $H^0_{at}(f)j = 62.941 - 0.1643\, \bar{H}^0_{at}(j)$ in kJ per g-atom; j corresponds to points 1–5.

(b) 1, BaO; 2, $BaCuO_2$; 3, Ba_2CuO_3; 4, $Ba_3Cu_5O_8$; 5, Ba_3CuO_4; 6, $Ba_2Cu_3O_5$; and 7, CuO. $H^0_{at}(f)j = -101.828 - 0.3681\, \bar{H}^0_{at}(j)$ per g-atom, j corresponds to points 1, 3 and 5; $H^0_{at}(f)\, i = 14.3435 + 0.1849\, \bar{H}^0_{at}(i)$ in kJ per g-atom, i corresponds to points 2, 4 and 7.

peratures and consequently the $\Delta H_{ph.tr.}$ values [4], as well as the average heat capacities of the phase transformation products [5], are only estimated values.

One of the most important thermochemical characteristics is the standard enthalpy of formation, which is presented in the following way [6]

$$\Delta H^0_{298}(j) = \Sigma m_i \Delta H^0_{298}(i) + \Delta H^0_{298}(\mathrm{ox})j \ (\mathrm{kJ\ mol^{-1}}) \qquad (2)$$

Table 2

Thermochemical properties of 17 complex oxides in the Y–Ba–Cu–O system

No.	Oxide	ΔH^0_{298}/kJ mol^{-1} [6]^b	S^0_{298}/J K^{-1} mol^{-1} [2]	$H^0_{298}-H^0_0$/ J mol^{-1} [1]	$C_p = a + b \times 10^{-3} T - c \times 10^5 T^{-2}$/ J K^{-1} mol^{-1} [3]			$T_{ph.tr}$/°C	$\Delta H_{ph.tr}$/J mol^{-1} [4]	$C_{p,ph.tr}$/J K^{-1} mol^{-1} [5]^a
					a	*b*	*c*			
1.	123-O6	−2586.8±7.9	319.86	49352	307.48	76.28	26.213	1373	1370	362.12
2.	123-O7	−2706.3±2.4	323.06	51107	315.29	54.47	42.450	1288	110900	418.10
3.	123.5-O7.5	−2794.5±3.5	345.15	54040	305.12	84.56	22.064	1190	23400	416.60
4.	124-O8	−2881.2±5.7	367.24	57750	356.72	45.74	42.470	1110	9200	445.80
5.	125-O9	−3055.2±10.5	411.42	65610	363.27	114.67	22.064	1023	8900	498.20
6.	143-O8.5	−3828.3±14.2	454.15	70016	312.96	41.07	42.810	1170	156500	357.90
7.	211-O5	−2712.0±2.6	223.00	35344	206.10	35.20	20.925	1543	31200	262.00
8.	$YCuO_2$	−1038.6±24.3	98.81	15677	92.90	16.36	8.050	1843	64500	125.60
9.	$Y_2Cu_2O_5$	−2214.8±5.1	200.83	31360	201.65	41.85	18.155	1428	1430	265.14
10.	Y_2BaO_4	−2533.5±0.7**	178.81	28128	164.65	20.53	20.320	1673	9800	198.37
11.	$Y_2Ba_2O_5$	−3131.0±6.4**	245.16	37905	227.88	22.05	36.734	1313	10200	249.27
12.	$Y_2Ba_4O_7$	−4314.1±7.5**	377.84	57346	335.28	24.60	52.440	1413	28100	386.75
13.	$Y_4Ba_3O_9$	−5666.6±9.3**	424.00	66049	393.75	48.23	44.915	2433	245700	51018
14.	$BaCuO_2$	−782.0±21.4**	110.52	17020	91.45	24.42	7.245	1318	28300	122.46
15.	$BaCu_2O_2$	−807.0±7.4	151.51	22707	118.30	27.09	8.010	1500	42800	163.76
16.	Ba_2CuO_3	−1409.1±29**	176.87	26730	145.32	28.77	16.594	1123	4300	176.00
17.	$BaCu_5O_8$	−2656.4±4.9**	420.00	65590	354.18	113.42	24.90	1073	3100	445.05

[a] Average heat capacity of the phase transformation products.

[b] ** ΔH^0_{298}(ox) data [6] corrected with the help of LAR [8].

where $\Delta H^0_{298}(i)$ and m_i are the standard enthalpy of formation and the number of moles of the ith simple oxide in the jth complex, respectively. $\Delta H^0_{298}(\text{ox})j$ is the standard enthalpy of formation of the jth complex oxide from simple ones.

For some phases, the $\Delta H^0_{298}(\text{ox})$ values have been found by following a multi-step approach [6]:

Table 3
Coefficients of the temperature polynomial, Eq. (5), approximating the reduced Gibbs energy of 17 phases in the Y–Ba–Cu–O system in J K^{-1} mol^{-1}

Oxide	Temperature interval/K	Coefficients φ_i in the Eq. (5)[a]				
		φ_1	φ_2	φ_3	φ_4	φ_5
123-O_6	298–1373	1055.14	307.48	−0.013107	5.44604	381.40
	>1373	1215.42	362.12	0	5.43031	0
123-O_7	298–1288	1075.33	315.29	−0.021225	5.9513	272.35
	>1288	1340.77	418.10	0	3.25552	0
247-O_{15}	298–1190	2148.74	610.241	−0.022064	9.60889	845.601
	>1190	2657.65	833.201	0	17.3158	0
124-O_8	298–1110	12.2622	356.72	−0.021235	6.48353	228.70
	>1110	1393.74	445.80	0	12.251	0
125-O_9	298–1023	1277.81	363.27	−0.011032	5.51401	573.351
	>1023	1577.56	498.201	0	12.2114	0
286-O_{17}	298–1170	2408.71	625.921	−0.04281	7.8871	410.701
	>1170	2878.43	715.801	0	−19.2508	0
211-O_5	298–1543	718.71	206.10	−0.010463	3.46586	176.0
	>1543	842.252	262.0	0	4.64533	0
$YCuO_2$	298–1843	322.883	92.9001	−0.004025	1.5435	81.8001
	>1843	410.752	125.6	0	−1.70203	0
$Y_2Cu_2O_5$	298–1428	684.934	201.65	−0.009078	3.66822	209.25
	>1428	806.223	265.14	0	8.19747	0
Y_2BaO_4	298–1673	575.058	164.65	−0.01016	2.86681	102.65
	>1673	642.195	198.37	0	4.53361	0
$Y_2Ba_2O_5$	298–1313	790.626	227.88	−0.018367	4.33092	110.25
	>1313	850.449	249.27	0	3.93898	0
$Y_2Ba_4O_7$	298–1413	1183.63	335.28	−0.02622	6.12571	123.0
	>1413	1288.84	386.75	0	7.76152	0
$Y_4Ba_3O_9$	298–2433	1373.93	393.75	−0.022458	6.85022	241.15
	>2433	1640.78	510.181	0	−3.85182	0
$BaCuO_2$	298–1318	329.0	91.4501	−0.003623	1.37476	122.1
	>1318	414.697	122.46	0	0.455881	0
$BaCu_2O_2$	298–1500	436.245	118.30	−0.004005	1.64372	135.45
	>1500	546.374	163.76	0	1.08169	0
Ba_2CuO_3	298–1123	524.179	145.32	−0.008297	2.34203	143.85
	>1123	597.379	176.0	0	3.3955	0
$Ba_3Cu_5O_8$	298–1073	1262.32	354.18	−0.01245	5.33475	567.101
	>1073	1499.96	445.05	0	8.01386	0

[a] φ_6 and φ_7 for all phases are equal zero.

(i) The exclusion of causal $\Delta H^0_{298}(\mathrm{ox})$ values for every complex oxide;

(ii) The calculation of a mean arithmetic $\Delta H^0_{298}(\mathrm{ox})$ value and average quadratic deviations;

(iii) The construction with the application of basic $\Delta H^0_{298}(\mathrm{ox})$ values of different complex oxides using

$$\Delta H^0_{298}(\mathrm{ox}) = (m_0, \Sigma N, \ln \Sigma N, \Sigma M \text{ and } \ln \Sigma M) \tag{3}$$

where m_0 is the number of oxygen atoms in the complex oxide molecule, ΣN is the sum of the element numbers (according to the Periodic System) in the complex oxide molecule, and ΣM is the sum of the atomic masses (molecular mass of complex oxide);

(iv) The calculation using Eqn. (3) of the mean arithmetic $\Delta H^0_{298}(\mathrm{ox})$ values and average quadratic deviations for every complex oxide. These $\Delta H^0_{298}(\mathrm{ox})_j$ values are viewed as the most reliable data.

The basic $\Delta H^0_{298}(\mathrm{ox})$ values [6] were taken for the following phases: 123–O_7 (many known initial $\Delta H^0_{298}(\mathrm{ox})$ data including 19 values), 123-O_6 [9], 124-O_8 [6], Y_2BaO_4 [7], $BaCuO_2$ [10], $Y_2Cu_2O_5$ [16], 211-0_5 [16], $Y_4Ba_3O_9$ [4], $BaCuO_3$ [2], 143-$O_{8.5}$ [2] and $YCuO_2$ [3].

The agreement of $\Delta H^0_{298}(\mathrm{ox})$ data for complex oxides in the Y_2O_3–BaO and BaO–CuO systems with the LAR [8] shows (Table 1 and Fig. 1) that the used methods [6] give enough reliable results. As can be seen from Table 1, the average differences between the $\Delta H^0_{298}(\mathrm{ox})$ values according Ref. [6] and the corrected ones are not more than ± 7%.

It is also worth noting that in all calculation procedures concerning Y-containing oxides we used the current value of $\Delta H^0_{298}(Y_2O_3)$, being -1919.4 kJ mol^{-1} [11]. In general we consider the data presented in Table 2 to be more correct than our previous estimations [17, 18].

For ease of application of individual compound thermochemical data is a thermodynamic simulation [16], the temperature-reduced Gibbs energy dependence for every complex oxide

$$\Phi_i^*(T) = \mathrm{Si}(T) - \{\Delta H^0_{298}(i) - [H^0_{298} - H^0_0](i)\}/T \quad \text{in J K}^{-1}\,\text{mol}^{-1} \tag{4}$$

is approximated with the help of the temperature polynomial [19]

$$\Phi_i^*(T) = \varphi_1 + \varphi_2 \ln x + \varphi_3 x^{-2} + \varphi_4 x^{-1} + \varphi_5 x + \varphi_6 x^2 + \varphi_7 x^3 \quad \text{in kJ K}^{-1}\,\text{mol}^{-1} \tag{5}$$

where φ_i are the numerical coefficients and $x = T \times 10^{-4}/\mathrm{K}$ (see Table 3).

4. Conclusion

Complete thermochemical properties for the main complex oxides of the Y–Ba–Cu–O system are presented. The values have been determined by analysing the known literature data with the help of various calculation methods. These data are more correct than our previous estimations published previously [17, 18]. The temperature-reduced Gibbs energy dependences for every complex oxide were also calculated.

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