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Estimation and revision of some thermodynamic data in the YBaCuO system.
Part 1. Values of $H^{\ominus}_{298} - H^{\ominus}_{0}$ and temperatures of the phase transformations

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Abstract

Analysing literature data for the YBaCuO system, the values of $H^{\ominus}_{298} - H^{\ominus}_{0}$, and the temperatures of melting and decomposition were estimated and empirical equations for their calculation are discussed. The values of these characteristic data for $YBa_2Cu_3O_7$ (123-O_7), $YBa_2Cu_3O_6$ (123-O_6), $YBa_2Cu_{3.5}O_{7.5}$ (123.5-$O_{7.5}$), $YBa_2Cu_4O_8$ (124-O_8), $YBa_2Cu_5O_9$ (125-O_9), $YBa_4Cu_3O_{8.5}$ (143-$O_{8.5}$), Y_2BaCuO_5 (211), $Y_2Cu_2O_5$ (202), $YCuO_2$ (101), Y_2BaO_4 (210), $Y_2Ba_2O_5$ (220), $Y_2Ba_4O_7$ (240), $Y_4Ba_3O_9$ (430), $BaCuO_2$ (011), $BaCu_2O_2$ (012), Ba_2CuO_3 (021) and $Ba_3Cu_5O_8$ (035) are given and discussed.

INTRODUCTION

We have estimated [1] the temperatures of melting and/or decomposition for a number of real and hypothetical compounds of the YBaCuO system, and also the enthalpy increments in the range 0–298 K.

The aim of this paper is to analyse the known experimental data, to try to find methods for calculation of $H^{\ominus}_{298} - H^{\ominus}_{0}$, and to evaluate the temperatures of the phase transformations including their correction and revision.

ANALYSIS OF THE LITERATURE DATA AND THE APPLICABILITY OF THE CALCULATION METHODS

Enthalpy increment at 0–298 K

Table 1 shows that the published $H^{\ominus}_{298} - H^{\ominus}_{0}$ ($\Delta_T H^{\ominus}$) are rather limited. For 123-O_7, however, the results allow the average arithmetic value of

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TABLE 1

The enthalpy increments $H^{\ominus}_{298} - H^{\ominus}_{0}$ of some compounds of the YBaCuO system compiled from the literature

Compound	$H^{\ominus}_{298} - H^{\ominus}_{0}$ in J mol^{-1}	Ref.	Remarks
123-O_7	50790	3	From experiment
	51426	4	From experiment
	51475	5	Calculation using empirical dependences
	51000	6	From experiment
	51350	7	From experiment
	51230	8	From experiment
	50790	8	From experiment
	50794	9	From experiment
	51107 ± 105		
123-O_6	51995	1	Calculation using empirical dependences
	49352	9	From experiment for 123-$O_{6.3}$
124-O_8	57750	7	From experiment
	56658	1	Calculation using empirical dependences
123.5-$O_{7.5}$	54040	10	From experiment
	57502	1	Calculation using empirical dependences
202	31360 ± 0.4	11	From experiment
	31992	1	Calculation using empirical dependences

$\Delta_T H^{\ominus}$ to be considered as a reliable characteristic. For the other compounds listed in Table 1, the $\Delta_T H^{\ominus}(\text{i})$ values calculated from experimental data seem more reliable than the calculated ones. Because such data are not available for the other phases, we used corrected standard entropy data for the compounds [2] to analyse the applicability of semi-empirical equations [12] for calculation of $\Delta_T H^{\ominus}(\text{i})$

$$H^{\ominus}_{298} - H^{\ominus}_{0} = 204\, S^{\ominus\prime}_{298} \exp(-S^{\ominus\prime}_{298}/98.277) \quad \text{in} \quad (\text{J mol}^{-1})/n \tag{1}$$

$$H^{\ominus}_{298} - H^{\ominus}_{0} = 216\, S^{\ominus\prime}_{298} \exp(-S^{\ominus\prime}_{298}/70.094) \quad \text{in} \quad (\text{J mol}^{-1})/n \tag{2}$$

where $S^{\ominus\prime}_{298}(\text{i}) = S^{\ominus}_{298}(\text{i})/n$, and n is the number of atoms in one molecule of the compounds.

Comparing experimental $\Delta_T H^{\ominus}(\text{i})$ values with those calculated from eqns. (1) and (2), it follows using eqn. (1) gives more correct results (see Table 2).

For the main compounds of the YBaCuO system, $\Delta_T H^{\ominus}(\text{i})$ values are calculated from eqn. (1) using the values of $S^{\ominus}_{298}(\text{i})$ that we obtained previously [2] (Table 3). The corrected values of the enthalpy increment at 0–298 K do not exceed by more than 4% the maximum deviations for those published in ref. 1.

TABLE 2

Comparison of the calculated and experimental enthalpy increment values

Compound	Experimental value $H^{\ominus}_{298} - H^{\ominus}_0$ in J mol^{-1}	Differences between $H^{\ominus}_{298} - H^{\ominus}_0$ values calculated from eqns. (1) and (2) [12] and experimental values in %	
		Eqn. (1)	Eqn. (2)
123-O_7	51107	+0.14	−3.7
123-O_6	49352	+0.80	−3.8
124-O_8	57750	+1.1	−2.7
123.5-$O_{7.5}$	54040	+1.4	−2.5
202	31360	+4.1	−1.1
		$\Delta = 1.51$	$\Delta = 2.8$

TABLE 3

Recommended $H^{\ominus}_{298} - H^{\ominus}_0$ values for the major compounds of the YBaCuO system and their comparison with the data in ref. 1

Compound	$H^{\ominus}_{298} - H^{\ominus}_0$ in J mol^{-1}	$\Delta(H^{\ominus}_{298} - H^{\ominus}_0)$/% from value recommended [1]
123-O_6	49352	+5.4
123-O_7	51107	+0.6
123.5-$O_{7.5}$	54040	+6.4
124-O_8	57750	−1.9
125-O_9	65610	–
211	35344	+5.1
202	31360	+2.0
143-$O_{8.5}$	70016	−2.9
101	15677	+5.2
210	28128	+3.4
220	37905	−4.1
240	57346	−4.8
430	66049	+3.8
011	17020	+4.4
021	26731	−5.1
035	65590	+8.0
012	22707	–

Temperatures of phase transformations

From Table 4 [13–18], three types of transformation can be discerned: incongruous melting (202, 011, 012, 211 and 123-O_7); congruous melting (101 and 430); and decomposition in the crystalline state (210, 220, 240, 021, 035, 124-O_8 and 123.5-$O_{7.5}$).

We have tried to find calculation methods for estimating the temperatures of these different transformations.

TABLE 4

Experimental data on the temperature of melting and/or decomposition of compounds in the YBaCuO system

Compound	T of phase transformation in K	Refs.	Remarks
210	1673	13–15	Decomposes with formation of 430 and Y_2O_3 in crystalline state
220	1313	13–15	Decomposes with formation of 210 and 240 in crystalline state
240	1413	13–15	Decomposes with formation of BaO and 430 in crystalline state
430	2433	13–15	Melts congruously
101	1843	15	Melts congruously
202	1428	13–15	Melts incongruously with formation of $Y_2O_3 + L$; melting temperature is assumed as mean arithmetic value of data given in ref. 13
011	1318	13	Melts with formation of oxygen
		15	Possible metling with decomposition into two immiscible liquid phases $L(BaO_x + BaO)$ and $L(CuO_x)$; melting temperature is recommended in ref. 13
012	1498 [a]	15	Melts with decompositon into two immiscible liquid phases L(Cu) and $L(BaO + CuO_x)$
021	1123	14	Decomposes with formation of 011 and BaO in crystalline state
035	1073	13, 14	Decomposes with formation of 011 and CuO in crystalline state
211	1543	13–15	Melts with formation of $Y_2O_3 + L$; melting temperature is recommended in ref. 13
123-O_7	1288	13–15	Melts with formation of $Y_2O_3 + L$ [13, 14] or with formation of $Y_2O_3 + 211 + L$ [15]; melting temperature is recommended in ref. 13
124-O_8	1123–1223 [a]	16, 17	Decomposes with formation of 123-O_7 + CuO in crystalline state at $P_{O_2} = 1$ bar
	1100 [a]		The same at atmospheric pressure
123.5-$O_{7.5}$	1234 [a]	17	Decomposes with formation of 123-O_7 + CuO in crystalline state at $P_{O_2} = 1$ bar
	1194 [a]	18	The same at atmospheric pressure

[a] For these phases, estimating the temperatures of transformations during calculations of the coefficients $\bar{K}$ was not considered.

Additive method

To estimate the temperatures of the phase transformations of complex oxides, the following equation has been suggested [19]

$$T_m = \bar{K} \sum N_i T_m(i) \tag{3}$$

where $\bar{K}$ is the empirical correlation coefficient for a group of similar substances with the same type of transformations, N_i is the mole fraction of the ith simple oxide in the complex compound, and $T_m(i)$ is the melting temperature of ith simple oxide.

Using eqn. (3), the melting temperatures of the oxides were taken from refs. 20–22, being 1509, 1609, 2977, 2193 and 723 K for Cu_2O, CuO, Y_2O_3, BaO and BaO_2, respectively.

The coefficient K in eqn. (3) was first estimated for each compound from the known value of $T_{ph.tr.}$, using the equation

$$K_i = T'_m(i) \Big/ \left(\sum N_i T_m(i)\right) \tag{4}$$

where $T'_m(i)$ is the experimental melting temperature of the ith compound, and $\Sigma N_i T_m(i)$ is the calculated value. For various compounds with the same sort of phase transformation, we grouped the K_i values and found the mean arithmetic value $\bar{K}$. Putting $\bar{K}$ in eqn. (3) we then calculated the temperatures, compared them with the experimental values and determined the deviations. At satisfactory convergence the estimation of unknown $T_{ph.tr.}$ values was approved.

Because the available information in the YBaCuO system refers only to the 101 and 430 congruous meltings, we considered it necessary to make further analyses of K_i for the other complex oxide compounds which also melt congruously.

The results of the estimation of $\bar{K}$ for the three types of phase transformations, together with the temperatures, calculated with using these coefficients in eqn. (3) are given in Table 5. It can be seen that there is a certain agreement between the experimental and calculated results, which allows the following equations to be applied

$$T_{IM} = 0.6973 \sum N_i T_m(i) \quad \text{(in K)} \tag{5}$$

$$T_{CM} = 0.9400 \sum N_i T_m(i) \quad \text{(in K)} \tag{6}$$

$$T_{DCS} = 0.5820 \sum N_i T_m(i) \quad \text{(in K)} \tag{7}$$

where IM, CM and DCS indicate incongruous and congruous melting, and decomposition in the crystalline state. Thus, it is possible to estimate the unknown transformation temperatures of the complex oxides.

TABLE 5

Coefficients $\bar{K}$ in eqn. (3) and results of the comparison of the temperatures of the phase transformations

Compound	$T_{\mathrm{ph.tr}}$ in K by experiment	K_i	$T_{\mathrm{ph.tr}}$ in K by eqn. (3) with coefficient $\bar{K}$	$\Delta(T_{\mathrm{ph.tr}})$/% by experiment and by eqn. (3) at $\bar{K}$
Incongruously melting compounds				
011	1318	0.6933	1326	+0.6
202	1428	0.6917	1439	+0.8
211	1543	0.6935	1574	−2.0
123-O_7	1288	0.7103	1264	−1.9
		$\bar{K} = 0.6973 \pm 0.006$		$\Delta = 1.315$
Congruously melting compounds				
430	2433	0.971	2358	−3.1
101	1843	0.893	1940	+5.3
Al_2TiO_5	2163	0.970	2100	−2.9
$Ba_3Al_2O_6$	2023	0.910	2092	+3.4
$BaTiO_3$	1978	0.912	2038	+3.0
Ba_2SiO_4	2033	0.955	2000	−1.6
$BaMoO_4$	1733	1.060	1533	−11.
$BaSiO_3$	1878	0.900	1968	+4.8
$CuFeO_2$	1470	0.902	1532	+4.2
$CuFe_2O_4$	1563	0.967	1520	−2.8
$BaWO_4$	1748	0.890	1850	+5.8
		$\bar{K} = 0.940 \pm 0.03$		$\Delta = 3.9$
Compounds decomposing in the crystalline state				
220	1313	0.514	1486	+13.2
210	1673	0.647	1504	−10.0
240	1413	0.600	1368	−3.2
021	1123	0.562	1163	+3.5
035	1073	0.587	1064	−0.85
		$\bar{K} = 0.582 \pm 0.005$		$\Delta = 6.2$

Estimation of melting temperatures from the known temperature dependence of the heat capacity of the compounds

According to ref. 20, the heat capacities of the crystalline compounds at the melting temperature (A_i) are equal to 32 ± 2.1 (J K^{-1} mol^{-1})/n, where n is the number of atoms in one molecule of compound.

Solving the equation

$$C_p = a + b \times 10^{-3}\,T - c \times 10^5 T^{-2} = A \quad \text{in} \quad (\mathrm{J\,K^{-1}\,mol^{-1}})/n \tag{8}$$

for known melting temperatures, the constant A_i can be calculated for each compound. For the group of substances with transformations of similar type, the mean arithmetic value $\bar{A}$ was found. Then, from the known dependence $C_p = f(T)$ and the determined value of $\bar{A}$, we calculated temperatures for every compound, compared them with experimental values and estimated deviations.

The necessary equations for $C_p = f(T)$ for the comopunds were taken from ref. 23, while those for the simple oxides was taken from ref. 21.

As before, for the estimation of a valid $\bar{A}$, we also analysed A_i for the group of congruously melting complex oxides. The results of the analysis are given in Table 6. Agreement between the calculated and experimental temperatures is in the 30% range.

Comparing the two above methods, it appears that the additive method (the melting temperatures of simple oxides being derived from empirical correlation coefficients obtained from experimental data for a group of similar compounds) is better for estimating unknown phase transformation

TABLE 6

Coefficients $\bar{A}$ in eqn. (8) and results of the comparison of the temperatures of the phase transformations

Compound	$T_{\text{ph.tr}}$ in K by experiment	$\bar{A}_i$ in $(\text{J K}^{-1}\,\text{mol}^{-1})/n$	$T_{\text{ph.tr}}$ in K by eqn. (8) at $\bar{A}$	$\Delta(T_{\text{ph.tr}})$/% experiment and by eqn. (8) at $\bar{A}$
Incongruously melting compounds				
011	1318	30.8055	1070	−18.9
220	1428	28.9230	1502	+5.9
211	1543	28.3740	1660	+7.6
123-O_7	1288	29.4520	1266	−4.8
		$\bar{A} = 29.39 \pm 0.52$		$\Delta = 9.2$
Congruously melting compounds				
430	2433	31.895	2196	−9.7
101	1843	29.400	2348	+32.8
Al_2TiO_5	2163	34.568	1658	−23.3
$Ba_3Al_2O_6$	2023	34.120	1516	−25.1
$BaTiO_3$ [a]	1978	(27.592)	(4065)	(+105.5)
Ba_2SiO_3	2033	30.106	2330	+14.6
$BaMoO_4$	1733	31.130	1727	−0.35
$BaSiO_3$	1878	29.137	2375	+26.4
$CuFeO_2$	1470	32.500	1280	−12.9
$CuFe_2O_4$	1563	30.607	1722	+10.2
$BaWO_4$	1748	30.600	1863	+6.6
		$\bar{A} = 31.40 \pm 0.73$		$\Delta = 16.2$

[a] For $T > 1800$ K, we did not find experimental $C_p = f(T)$ data for $BaTiO_3$ or TiO_2. Extrapolation of $C_p = f(T)$ (298–1800 K) to higher temperatures is probably not valid and leads to low values of $C_p(T_m)$ and great differences between the results of experiment and calculation. In the calculation of Δ, data for $BaTiO_3$ were not taken into account.

TABLE 7

Temperatures of phase transformations of some compounds in the YBaCuO system; the most reliable values are underlined

Compound	$T_{\text{ph.tr.}}$ in K (type) by experiment DCS	$T_{\text{ph.tr}}$ in K, calculation by eqns. (5)–(7)			T_{CM} in K, by ref. 1
		IM	CM		
123-O_6	– (IM)	–	1373	–	1446
123-$O_{7-\delta}$	1288 (IM)	–	1264	–	1503
123.5-$O_{7.5}$	1190 (DCS)	1045	–	–	1645
124-O_8	1100 (DCS)	1037	–	–	1715
125-O_9	– (DCS)	1023	–	–	–
143-$O_{8.5}$	– (DCS)	1170	–	–	1276
211	1543 (IM)	–	1574	–	1545
202	1428 (IM)	–	1440	–	1500
101	1843 (CM)	–	–	1940	1560
210	1673 (DCS)	1504	–	–	1610
220	1313 (DCS)	1486	–	–	1525
240	1413 (DCS)	1369	–	–	1400
430	2433 (CM)	–	–	2358	1555
012	1500 (IM)	–	1290	–	–
021	1123 (DCS)	1163	–	–	1360
035	1073 (DCS)	1064	–	–	1011
011	1318 (IM)	–	1326	–	1280

Key: DCS, decomposition in crystal state; IM, incongruous melting; CM, congruous melting.

temperatures of complex oxides. From the literature data [13–18, 24, 25], it would appear that the phases 125-O_9 and 143-$O_{8.5}$ could decompose in the crystalline state, whereas 123-O_6 melts incongruously. The results for $T_{\text{ph.tr}}$ derived from eqns. (5)–(7) for compounds of the YBaCuO system are given in Table 7, together with experimental data and data from ref. 1. The values of $T_{\text{ph.tr.}}$ which seem to us to be most correct are underlined.

These data, however, are different from those published previously [1] because in that study the type of phase transformation was not taken into account and all the compounds were considered to melt congruously.

DISCUSSION

The experimental and calculated data for the temperatures of the phase transformations should not be considered as being definitive. The YBaCuO system is very complicated, and only its phase diagram has been continuously studied [13–18]. The literature data [13, 15, 18, 26–28] show that practically all the phases in this system lose oxygen with increasing temperature. This is accompanied by a change in the composition of the complex oxides, and by transformations with formation of new compounds and solutions. The experimental data given in Table 4 were obtained at different partial pressures of oxygen, with varying initial compositions, and experimental methods and, probably, in non-equilibrium conditions for a number of compounds. Thus, the phase transformation temperature data should be regarded as preliminary information for the upper regions of phase existence.

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