ESTIMATION OF MELTING (DECOMPOSITION) HEAT OF SOME COMPOUNDS IN THE Y–Ba–Cu–O SYSTEM

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Abstract

A thermodynamical method for the estimation of decomposition heat in a crystal state, incongruous and congruous melting of compounds with the use of temperature dependencies of total entropies of compounds was suggested. Entropies and heats of phase transformation of $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$, $YBa_4Cu_3O_{8.5}$, Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, $Y_4Ba_3O_9$, $YCuO_2$, $Y_2Cu_2O_5$, Y_2BaCuO_5, Ba_2CuO_3, $BaCuO_2$, $BaCu_2O_2$, $Ba_3Cu_5O_8$ were calculated. Data, obtained by the authors earlier, are discussed.

Keywords: congruous melting, incongruous melting, superconductors, thermodynamical method, Y–Ba–Cu–O system

Introduction

No experimental data for heats of melting (decomposition) of compounds in the Y–Ba–Cu–O system can be find only estimating calculations are given in [1]. The aim of our contribution is to develop a calculation method for estimating heats of congruous, incongruous melting (*CM* and *IM*) and decomposition in a crystal state (*DCS*) for complex oxide compounds; it can be applied for the estimation of heats of phase transformations of $YBa_2Cu_3O_6$ (123-O_6), $YBa_2Cu_3O_7$ (123-O_7), $YBa_2Cu_{3.5}O_{2.5}$ (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), $YCuO_2$, Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, $Y_4Ba_3O_9$, $BaCu_2O_2$, Ba_2CuO_3, $Ba_3Cu_5O_8$ and $BaCuO_2$.

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Methods for calculation of ΔS and ΔH phase transformation

Let us consider 1 g-mole of a hypothetical oxide $A_aB_bC_cO_y$, for which a type of phase transformation and its temperature are unknown. Assuming the following schemes:

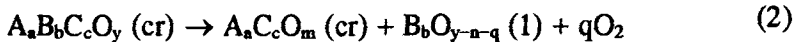### *Decomposition in the crystal state (DCS)*

It is represented by the reaction,

$$A_aB_bC_cO_y \text{ (cr)} \rightarrow A_aB_n \text{ (cr)} + B_bC_cO_{y-n} \text{ (cr)} \tag{1}$$

described in an arbitrary way (similarly to the following Eqs (2–4).

Incongruous melting (IM)

(i) Reaction with formation of one crystal compound, melt and possible secretion of oxygen,

$$A_aB_bC_cO_y \text{ (cr)} \rightarrow A_aC_cO_m \text{ (cr)} + B_bO_{y-n-q} \text{ (l)} + qO_2 \tag{2}$$

or (ii) reaction corresponding to 2 phases separated liquids and possible secretion of oxygen,

$$A_aB_bC_cO_y \text{ (cr)} \rightarrow A_aO_n \text{ (l)} + B_bC_cO_{y-n-q} \text{ (l)} + qO_2 \tag{3}$$

Congruous melting (CM)

$$A_aB_bC_cO_y \text{ (cr)} \rightarrow A_aB_bC_cO_y \equiv A_aO_n \text{ (l)} + B_bO_p\text{(l)} + C_cO_{y-n-q} \text{ (l)} \tag{4}$$
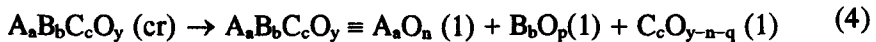
i.e., the reaction without liquid formation nor mixing phases and secretion of oxygen.

It is highly probable, that in a general case the changes in entropy and energy consumptions per 1 g-atom of a hypothetical complex oxide will be the highest one at *CM* and the lowest one at *DCS*, which means

$$\Delta S_{CM}^{at} > \Delta S_{IM}^{at} > \Delta S_{DCS}^{at} \tag{5}$$

or

$$\Delta S_{CM}^{at} T_{CM} > \Delta S_{IM}^{at} \cdot T_{IM} > \Delta S_{DCS}^{at} \cdot T_{DCS} \tag{6}$$

Besides, possible sequence of phase transformations can obey the succession

$$T_{CM} > T_{IM} > T_{DCS}\text{'} \tag{7}$$

(valid in the case that the type and temperature of phase transformation of a hypothetical compound are unknown) as follows from analysis of state diagrams and reference literature [2–6].

Estimation of $\Delta H_{\text{ph.tr.}}$ at the assumption $\Delta S_{\text{ph.tr.}} \cong const$

Considering comparable changes of entropy at various phase transformations, or

$$\Delta S_{\text{CM}} \cong \Delta S_{\text{IM}} \cong \Delta S_{\text{DCS}} \tag{8}$$

and taking in account only the temperature of transformation of a definite compound, then a rough estimation of heats of phase transformations can be calculated by the equations:

$$\Delta H_{\text{CM}} \cong \Delta S_{\text{CM}} \cdot T_{\text{CM}}' \tag{9}$$

$$\Delta H_{\text{IM}} \cong \Delta S_{\text{IM}} \cdot T_{\text{IM}}' \tag{10}$$

$$\Delta H_{\text{DCS}} \cong \Delta S_{\text{DCS}} \cdot T_{\text{DCS}}' \tag{11}$$

The value of ΔS_{CM} of complex oxide can be estimated by empiric dependency [7],

$$\Delta S_{\text{CM}} \cong \sum n_i(\text{ox}) \cdot \Delta S_{\text{CM}}(\text{ox}), \tag{12}$$

where n_i (ox) is a number of moles in a simple i-th oxide in complex one, ΔS_{CM} (ox) is the change of entropy during melting of i-th simple oxide.

For simple oxides the necessary data are available in Ref. [6]. For complex oxides of the Y–Ba–Cu–O system temperatures and variants of phase transformation are taken from Ref [8]. Results of calculation from the Eqs (9–12) are given in Table 1 (I. variant).

Thermodynamic method

Taking into account that $\Delta S_{\text{CM}} \neq \Delta S_{\text{IM}} \neq \Delta S_{\text{DCS}}$ we can consider following cases:

Decomposition in crystal state

Here we can calculate the entropy change of reaction (1) at $T = T_{\text{DCS}}$:

$$\Delta_r S = S_f(T)[\text{A}_a\text{O}_n(\text{cr})] + S_f(T)[\text{B}_b\text{C}_c\text{O}_{y-n}(\text{cr})] - S_f(T)[\text{A}_a\text{B}_b\text{C}_c\text{O}_y(\text{cr})], \tag{13}$$

Table 1 Characteristics of phase trasformations if the main compounds in the Y-Ba-Cu-O system

$N^{\circ}_{=}$	Compound	Type of trans- formation and T/K, Ref. [8]		I. variant		II. variant			Characteristics of melting		
				$\Delta S_{ph.tr.}$ / $J \cdot K^{-1} \cdot mole^{-1}$	$\Delta H_{ph.tr.}$ / $kJ \cdot mole^{-1}$	$\Delta S_{ph.tr.}$ / $J \cdot K^{-1} \cdot mole^{-1}$	$\Delta H_{ph.tr.}$ / $kJ \cdot mole^{-1}$	T_{CM} / K	ΔS_{CM} / $J \cdot K^{-1} \cdot mole^{-1}$	ΔH_{CM} / $kJ \cdot mole^{-1}$
1	$YCuO_2$	CM	1843	38.8	71.5	35.0	64.5	1560	31.5	54.8
2	$Y_4Ba_3O_9$	CM	2433	149.2	363.0	101.0	245.7	1555	140.5	218.5
3	$123-O_6$	IM	1373	170.0	233.3	$0+1$	$0+1.37$	1446	105.4	152.4
4	$123-O_7$	IM	1288	95.5	123.0	86.1	110.9	1503	141.2	171.6
5	Y_2BaCuO_5	IM	1543	68.8	106.1	20.2	31.2	1545	79.0	122.1
6	$Y_2Cu_2O_5$	IM	1428	49.8	71.1	$0+1$	$0+1.43$	1500	79.0	118.6
7	$BaCu_2O_2$	IM	1498	68.9	103.3	28.2	42.8	–	–	–
8	$BaCuO_2$	IM	1318	33.6	44.4	21.5	28.3	1280	35.1	44.9
9	$123.5-O_{7.5}$	DCS	1190	99.2	118.0	19.6	23.4	1645	123.0	202.2
10	$124-O_8$	DCS	1110	102.9	114.2	8.3	9.2	1715	131.7	225.9
11	$125-O_9$	DCS	1023	110.2	112.7	8.6	8.9	–	–	–
12	$143-O_{8.5}$	DCS	1170	144.8	169.5	133.7	156.5	1276	145.0	185.0
13	Y_2BaO_4	DCS	1673	61.5	102.8	5.8	9.8	1610	61.5	99.0
14	$Y_2Ba_2O_5$	DCS	1313	87.8	115.2	7.8	10.2	1525	79.0	120.5
15	$Y_2Ba_4O_7$	DCS	1413	140.4	198.4	19.9	28.1	1400	114.2	159.8
16	Ba_2CuO_3	DCS	1123	60.0	67.3	3.9	4.3	1360	52.7	71.7
17	$Ba_3Cu_5O_8$	DCS	1073	115.6	124.0	2.9	3.1	1011	140.5	142.1

where $S_f(T)$ is the temperature dependency of total entropy of i-th compound; $\Delta_r S$ of this reaction can be substituted by ΔS_{DCS}.

Incongruous melting

We then calculate the change of entropy of reaction (2) or (3) at $T = T_{IM}$; and $\Delta_r S$ is substituted by ΔS_{IM}. For example, for reaction (2) is

$$\Delta_r S = S_f(T)[A_a C_c O_m(cr)] + S_f(T)[B_b O_{y-m-q}(1)] + q \cdot S_f(T)[O_2] -$$

$$- S_f(T)[A_a B_b C_c O_y(cr)]. \tag{14}$$

The temperature dependence of total entropy of the i-th substance in liquid state is assumed to be equal to

$$S_f(T)[i(1)] \cong S_f[i(cr)] + \Delta S_{CM}(i) \tag{15}$$

where $S_f(T)[i(cr)]$ is calculated at $T = T_{IM}$, and $\Delta S_{CM}(i)$ is the change of entropy at congruous melting point of the i-th substance.
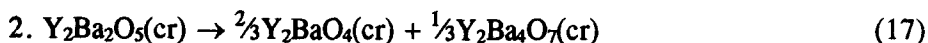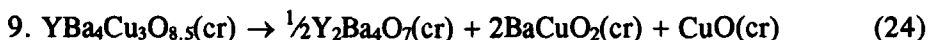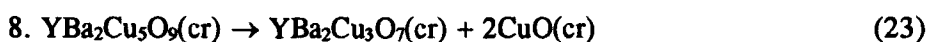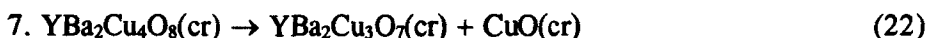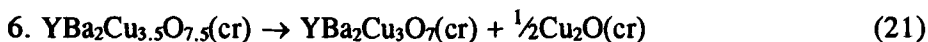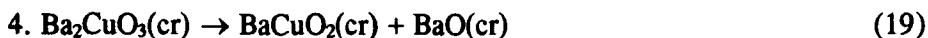
Congruous melting

The entropy change of reaction (4) is calculated for phases in the liquid state where the temperature functions of total entropy is found through Eq. (15). For determining an estimate of the $S_f(T)[i]$ functions of respective compounds in the Y−Ba−Cu−O system we can take values of S_{298}^o from Ref. [9]; temperature dependency of heat capacities of compounds in the Y−Ba−Cu−O system by Ref. [10]. For the rest of compounds, copper and oxygen in Ref. [6]. The entropy changes at the melting point of simple oxides CuO, Cu$_2$O, BaO, BaO$_2$ and Y$_2$O$_3$ were taken equal 7.33; 42.54; 26.32; 33.0 and 35.13 J/K·mole [6], respectively. For the better illustration the temperature dependency of entropy for some substances are listed in Table 2.

Reactions for calculation of $\Delta_r S$

The reactions are built on the base of data, given in [2–5, 8].

Decomposition in crystal state

1. $Y_2BaO_4(cr) \rightarrow \frac{1}{3}Y_2O_3(cr) + \frac{1}{3}Y_4Ba_3O_9(cr)$ (16)

2. $Y_2Ba_2O_5(cr) \rightarrow \frac{2}{3}Y_2BaO_4(cr) + \frac{1}{3}Y_2Ba_4O_7(cr)$ (17)

3. $Y_2Ba_4O_7(cr) \rightarrow \frac{5}{2}BaO(cr) + \frac{1}{2}Y_4Ba_3O_9(cr)$ \hfill (18)

4. $Ba_2CuO_3(cr) \rightarrow BaCuO_2(cr) + BaO(cr)$ \hfill (19)

5. $Ba_3Cu_5O_8(cr) \rightarrow 3BaCuO_2(cr) + 2CuO(cr)$ \hfill (20)

6. $YBa_2Cu_{3.5}O_{7.5}(cr) \rightarrow YBa_2Cu_3O_7(cr) + \frac{1}{2}Cu_2O(cr)$ \hfill (21)

7. $YBa_2Cu_4O_8(cr) \rightarrow YBa_2Cu_3O_7(cr) + CuO(cr)$ \hfill (22)

8. $YBa_2Cu_5O_9(cr) \rightarrow YBa_2Cu_3O_7(cr) + 2CuO(cr)$ \hfill (23)

9. $YBa_4Cu_3O_{8.5}(cr) \rightarrow \frac{1}{2}Y_2Ba_4O_7(cr) + 2BaCuO_2(cr) + CuO(cr)$ \hfill (24)

However, we have to draw attention to following points. For the reactions (16–23) there are experimental foundations [2–5, 8] while for the reaction (24) there are none. It was the reason why we have to analyze several possible variants of 143-$O_{8.5}$ decomposition. We can chose the reaction (24) where $\Delta_r S$ is the smallest one. The following conditions were taken into account: (i) temperatures of phase transformations of decomposition products must be higher than the T of decomposition of 143-$O_{8.5}$; (ii) reaction must proceed without any secretion of oxygen because at 1170 K (when calculating T_{DCS} 143-$O_{8.5}$ [8]) the transformation of Cu(II)O $\rightarrow$ Cu(I)$_2$O accompanied with oxygen secretion does not occur [2]. There, however, is no a full confidence in real existence of this phase as an individual substance because it is thermodynamically unstable according to Ref. [2].

Incongruous melting

For reactions of this type of transformation we could give preliminary explanations. According to the phase diagram give in [2], CuO(cr) melts at 1348 K; within 1348–1373 K there exist the CuO melt and within 1373–1673 K the melt of Cu$_2$O with oxygen according to the reaction

$$CuO(l) \rightarrow \frac{1}{2}Cu_2O(l) + \frac{1}{4}O_2. \qquad (25)$$
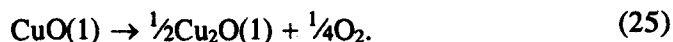
Crystalline Cu$_2$O melts with disproportioning at 1473 K according to the possible reaction

$$Cu_2O(cr) \rightarrow Cu(l) + CuO(l). \qquad (26)$$
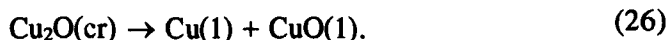
Since T_{IM} of Cu-containing compounds of the Y–Ba–Cu–O system can lay within temperature ranges of the existence of Cu-oxides with the valence (I) and

(II), reactions (25) or (26) should be considered for the calculation of $\Delta_r S_{IM}$ of complex oxides.

It should be also noted that the temperature difference of experimental data of compounds for phase transformations can be considerable. For example, for the T_{IM} the data $Y_2Cu_2O_5$ by data of different researchers varies within 1120–1180°C, and for 123-O_7 within 925–1300°C.
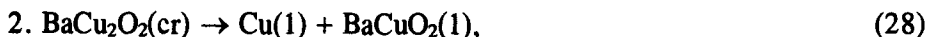
We should not assume that temperatures of transformations (25) and (26) are perfectly correct. As proved by experiment [8], we had to calculate for some compounds several variants of reactions regarding in particular, copper oxides (I) and (II). As the appropriate value of $\Delta_r S$ was taken the smallest value from $\Delta_r S$ series of considered reactions.

Experimental estimation of $T_{ph.tr.}$ has to be done, as a rule, in air at total atmospheric pressure [8]. Thus, we should consider the calculated characteristic of *IM* (as well as *DCS* and *CM*) under the same conditions.
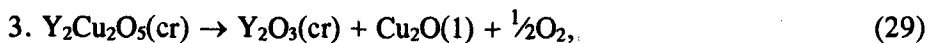
With regard to these conditions where reactions of incongruous melting were built it follows

$$1. \ BaCuO_2(cr) + \tfrac{1}{2}O_2 \rightarrow \left\{\tfrac{1}{2}BaO_2(l) + \tfrac{1}{2}BaO(l)\right\} + CuO(l) \tag{27}$$
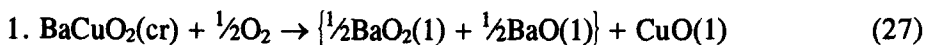
where it is assumed that two liquid phases $\{BaO_2(l) + BaO(l)\}$ and $CuO(l)$ do not mix;

$$2. \ BaCu_2O_2(cr) \rightarrow Cu(l) + BaCuO_2(l), \tag{28}$$

where melts of Cu and $BaCuO_2$ do not mix;

$$3. \ Y_2Cu_2O_5(cr) \rightarrow Y_2O_3(cr) + Cu_2O(l) + \tfrac{1}{2}O_2, \tag{29}$$

$$4. \ Y_2BaCuO_5(cr) \rightarrow Y_2O_3(cr) + BaCuO_2(l), \tag{30}$$

$$5. \ YBa_2Cu_3O_7(cr) \rightarrow \tfrac{1}{2}Y_2O_3(cr) + \left\{2BaCuO_2(l) + CuO(l)\right\} + \tfrac{1}{4}O_2 \tag{31}$$

$$6. \ YBa_2Cu_3O_6(cr) \rightarrow \tfrac{1}{2}Y_2O_3(cr) + [2BaCuO_2(l) + \tfrac{1}{2}CuO(l). \tag{32}$$

As this value of ΔS_{CM} ($BaCuO_2$) for reactions (28, 30–32) was taken $\Delta_r S$ fron the reaction (27).

Congruous melting

$$1. \ YCuO_2(cr) \rightarrow \tfrac{1}{2}Y_2O_3(l) + \tfrac{1}{2}Cu_2O(l), \tag{33}$$

$$2. \ Y_4Ba_3O_9(cr) \rightarrow 2Y_2O_3(l) + 3BaO(l). \tag{34}$$
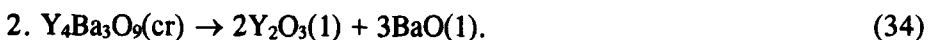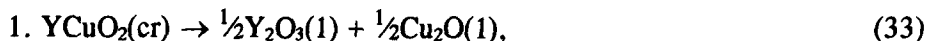
After estimating $\Delta S_{ph.tr.}$, taking $T_{ph.tr.}$ by [8], we calculated heats of transformations by the known formula,

$$\Delta H_{ph.tr.} = \Delta S_{ph.tr.} \cdot T_{ph.tr.} \tag{35}$$

Empiric estimation of ΔS_{CM} and ΔH_{CM}

In Refs [12–14] it was shown that ΔS_{CM} per 1 g-atom (ΔS_{CM}^{at}) for groups of the similar substances yield similar values. From Ref. [14] follows that for compounds of the Y–Ba–Cu–O system $\Delta S_{CM}^{at} = 8.782$ J/K·g-atom, and calculation of ΔH_{cm} was worked out on the bases of equation,

$$\Delta H_{CM} \cong \Delta S_{CM}^{at} \cdot T_{CM} \cdot n, \tag{36}$$

where n is the number of atoms in a molecule of compound. By Ref. [1] and under the assumption that all compounds listed in Table 1 melt congruously, according to Eq. (35) $\Delta H_{ph.tr.}$ was calculated. But, as it became known from the subsequent analysis [8], only $YCuO_2$ and $Y_4Ba_3O_9$ melt congruously, and only for them results of calculations of ΔS_{CM} are of interest.

Discussion of results

From the three methods shown for estimating the changes of entropies (and consequently the heats of phase transformations) the most correct one seems to be the thermodynamic method marked as variant 2. The values of $S_{298}^{o}(i)$ and functions $C_p(i) = f(T)$, taken from Refs [9, 10] were found corrected on the bases of data analysis obtained by a number of researchers. Consequently the functions of total entropy of compounds (Table 2) can be considered as satisfactorily reliable.

The validity of $\Delta S_{ph.tr.}$ and $\Delta H_{ph.tr.}$ estimation will predominantly depend, on the reliability of finding temperatures and types of phase transformations, as well as on the accuracy of reaction stoichiometry and the assumptions of calculations.

On these bases the mentioned above, we made a more detailed analysis of the results for $\Delta S_{ph.tr.}$ ($\Delta H_{ph.tr.}$) estimation only for the phase 143-$O_{8.5}$ (Table 1.).

In the group of substances with congruous type of melting ΔS_{CM}^{at} is in average of 7.525 J/K·g-atom; for uncongruously melting compounds it is in average of 3.34 J/K·g-atom and for compounds, decomposing in crystal state ΔS_{CM}^{at} is abuot 0.815 J/K·g-atom (Table 3).

Thus, in the row of transformations: $CM \rightarrow IM \rightarrow DCS$ we can observe a decrease of the $\Delta S_{ph.tr.}^{at}$ values as estimated by an approximate ratio 9.2:4.1:1. Similar analysis for $\Delta H_{ph.tr.}$ and $T_{ph.tr.}$ leads for the analogous sequences of trans-

formation types as corresponding to the ratios 15:8.15:1 and 1.72:1.14:1 (Table 3).

In conclusion this is in agreement with our consideration, expressed earlier, however, with certain exclusions. Beyond the *IM*-compounds these are phases 123-O_6 and $Y_2Cu_2O_5$ for which $\Delta S_{IM} \cong 0$, i.e. below that for the compounds decomposing in crystal state. It may indicate a low strength of connection between Y_2O_3 and a residual oxide part in these phases.

Table 2 Coefficients in equation S_f $(T) = A' \cdot 10^{-3} T + A'' \cdot \ln$ $(T) + A''' \cdot 10^5 \cdot T^{-2} - B(B')$, J/K·mole, of the entropy from 298 K to T(B) and of total entropy of substances of the Y–Ba–Cu–O system

N$_{\underline{o}}$	Substances	Coefficients				
		A'	A''	A'''	B'	B''
1	2	3	4	5	6	7
1	O_2	4.20	30.00	0.84	173.1	−31.8
2	Cu(cr)	6.28	22.65	0	130.9	97.5
3	BaO(cr)	4.35	53.28	4.15	309.5	239.2
4	BaO_2(cr)	8.36	56.88	0	326.5	231.9
5	Cu_2O(cr)	23.94	62.30	0	362.0	269.0
6	CuO(cr)	20.10	38.80	0	226.9	184.2
7	Y_2O_3(cr)	7.20	122.15	9.62	708.8	609.7
8	123-O_7	54.50	315.30	21.20	1836.3	1513.2
9	123-O_6	76.30	307.50	13.11	1789.2	1469.3
10	124-O_8	45.74	356.70	21.24	2069.7	1702.5
11	123.5-$O_{7.5}$	84.56	305.10	11.03	1775.9	1393.1
12	143-$O_{8.5}$	41.10	313.00	21.40	1819.2	1365.0
13	125-O_9	144.70	363.30	11.03	2116.1	1704.7
14	Y_2BaCuO_5	35.2	206.10	10.46	1196.5	973.5
15	$Y_2Cu_2O_5$	41.80	201.70	9.10	1166.1	965.3
16	$YCuO_2$	16.40	92.90	4.00	538.7	439.9
17	Y_2BaO_4	20.50	164.50	10.20	955.5	776.7
18	$Y_2Ba_2O_5$	22.05	227.90	18.40	1325.5	1080.3
19	$Y_4Ba_3O_9$	48.20	393.80	22.50	2282.9	1858.9
20	$Y_2Ba_4O_7$	24.60	335.30	26.20	1946.9	1569.0
21	$BaCuO_2$	24.40	91.50	3.60	532.4	422.0
22	$BaCu_2O_2$	27.10	118.30	4.00	686.6	535.1
23	Ba_2CuO_3	28.80	145.30	8.30	845.8	668.9
24	$Ba_3Cu_5O_8$	113.40	354.20	12.50	2065.6	1645.4

Table 3 Characteristics of phase transformations for compounds of the Y–Ba–Cu–O system per 1 g-atom (variant II.)

$N^{\circ}_{=}$	Compound	Type of transformation Ref. [8]	Characteristics of transformation		
			T/K Ref. [8]	ΔS / $J \cdot K \cdot g\text{–atom}^{-1}$	ΔH / $kJ \cdot g\text{–atom}^{-1}$
1	2	3	4	5	6
1	$YCuO_2$	CM	1843	8.75	16.12
2	$Y_4Ba_3O_9$	CM	2433	6.30	15.35
		average	2138	7.53	15.74
3	123-O_6	IM	1373	0.08	0.11
4	123-O_7	IM	1288	6.62	8.53
5	Y_2BaCuO_5	IM	1543	2.20	3.47
6	$Y_2Cu_2O_5$	IM	1428	0.11	0.16
7	$BaCu_2O_2$	IM	1498	5.64	8.56
8	$BaCuO_2$	IM	1318	5.38	7.08
		average	1408	3.43	4.65
9	123.5-$O_{7.5}$	DCS	1190	1.40	1.67
10	124-O_8	DCS	1110	0.55	0.61
11	125-O_8	DCS	1023	0.51	0.52
12	Y_2BaO_4	DCS	1673	0.83	1.40
13	$Y_2Ba_2O_5$	DCS	1313	0.87	1.13
14	$Y_2Ba_4O_7$	DCS	1413	1.53	2.16
15	Ba_2CuO_3	DCS	1123	0.65	0.72
16	$Ba_3Cu_5O_8$	DCS	1074	0.20	0.20
		average	1240	0.82	1.05
17	143-$O_{8.5}$	DCS	1170	8.10	9.48

For 143-$O_{8.5}$ the ΔS_{DCS} and ΔH_{DCS} values are considerably different from those for other *DCS*-phases.

What can be considered as realistic is that the orthorhombic phase 123-$O_{7-\delta}$ (in limit 123-O_7) is metastable [11, 15, 16]. The time of decomposition, however, is probably too long and this allows to estimate experimentally T_{IM}. Thus our results can be considered as an additional confirmation of strength and stability of 123-O_7 at high temperatures, particularly as the $\Delta S_{IM}^{at} = 6.62$ value is higher than that for the rest of *IM*-compounds and of superconductors. Under equilibrium heating transformation and loss of oxygen [16] occur so that we can estimate characteristic of the tetragonal phase 123-$O_{7-\delta}$ (in limit 123-O_6). Consequently, as the 123-O_7 and other superconductors of this homologic row are considered metastable (reaching probably, even 124-O_8 [11]) we can estimate

non-equilibrium characteristics of phase transformations being useful for practical purposes.

Out of DCS phases i.e. $247\text{-}O_{15}$, $124\text{-}O_8$ and $125\text{-}O_9$ the most stable is $123.5\text{-}O_{7.5}$. This agrees with our preliminary estimation of thermodynamic stability of this phase see Ref. [11].

Some comments about characteristics of phase transformations received by variant I and in [1] and possibility of their applications. From Table 1. It can be seen that for the CM-compounds $YCuO_2$ and $Y_4Ba_3O_9$ calculated by I, II variants and in analogy with Ref. [1] we achieved certain agreement while for the rest of transformation types the agreement can be considered only incidental. Since for new phases no characteristics of phase transformations are known, it is expedient for preliminary estimation. These methods are oriented to maximum changes of entropies of phase transformations of different and yet unknown types Appearance of additional data will allow one to correct this information, especially for IM and DCS of compounds.

<div align="center">* * *</div>

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Zusammenfassung — Unter Zuhilfenahme der Temperaturabhängigkeit der Gesamtentropie von Verbindungen wird eine thermodynamische Methode zur Schätzung der Zersetzungswärme im kristallinen Zustand, beim inkongruenten und kongruenten Schmelzen von Verbindungen vorgeschlagen. Es wurden die Entropien und Phasenumwandlungswärmen von $YBa_2Cu_3O_6$, $YBa_2Cu_3O_7$, $YBa_2Cu_{3.5}O_{7.5}$, $YBa_2Cu_4O_8$, $YBa_2Cu_5O_9$, $YBa_4Cu_3O_{8.5}$, Y_2BaO_4, $Y_2Ba_2O_5$, $Y_2Ba_4O_7$, $Y_4Ba_3O_9$, $YCuO_2$, $Y_2Cu_2O_5$, Y_2BaCuO_5, Ba_2CuO_3, $BaCuO_2$, $BaCu_2O_2$, $Ba_3Cu_5O_8$ berechnet. Frühere Angaben von anderen Autoren werden diskutiert.