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APPLICATION OF MODEL OF IDEAL SOLUTION OF INTERACTION PRODUCTS (ISIP) AND THERMODYNAMIC MODELING (TM) FOR DESCRIPTION OF SUPERCONDUCTING PHASES IN THE SYSTEM YBaCuO

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Abstract

The thermochemical properties of Cu_2O_3 were calculated. The stability of Cu_2O_3 was studied with the help of TM methods. It was shown that this oxide can exist in oxygen atmosphere ($P=10^5$ Pa) at temperatures below 380 K.

A variant of the ISIP model was used with TM to determine the Cu^+, Cu^{2+} and Cu^{3+} contents and oxygen indexes in $YBa_2Cu_3O_x$ (123-O_x), $YBa_2Cu_{3.5}O_y$ (123.5-O_y), $YBa_2Cu_4O_z$ (124-O_z), $YBa_2Cu_5O_q$ (125-O_q) and $YBa_2Cu_6O_m$ (126-O_m) solutions at 100–1200 K in oxygen medium ($P=10^5$ Pa).

Methods for determination of some thermodynamic properties and oxygen indices are suggested for a superconductor family in the system YBaCuO.

Keywords: modeling, solution, system YBaCuO, thermodynamic properties

Introduction

Different solution models have been proposed to describe the superconducting phase 123-O_x (see, for example, [1–4]). As a rule, their application permits evaluation of the changes in the oxygen index in the formula of this phase under various conditions (temperature/pressure changes, interaction with different substances, etc.). These solution models were put forward after determination (or estimation) of the main thermochemical properties (standard enthalpy, entropy and heat capacity) for the phases 123-O_7 and 123-O_6. The essence of the models is described in the original papers.

In 1988 [2], when the thermodynamic properties of the phase 123-O_x were practically unknown, we attempted to use the ISIP model and TM methods to describe the conditions of synthesis of the phase 123-O_7. The initial components of the solution were Cu_2O, CuO and Cu_2O_3. For Cu_2O_3 the thermochemical properties were evaluated by calculation methods [2], but in some cases, and in particular the standard enthalpy, the calculations yielded uncertain results.

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The goals of the present work were (i) a revision of the thermochemical properties of Cu_2O_3, and investigation of its stability; (ii) application of the ISIP model with TM for determination of the Cu^+, Cu^{2+} and Cu^{3+} contents and oxygen indices in 123-O_x, 123.5-O_y, 124-O_z, 125-O_q and 126-O_m solutions with use of the revised Cu_2O_3 properties; and (iii) an attempt to use the data obtained from computer investigations with model solutions to evaluate some properties of real superconductors in the system YBaCuO.

Methods and procedures

Thermodynamic simulation was carried out with the help of TM methods, the program ASTRA-4 and the data bases ASTRA and ASTRA.OWN [5].

For Cu_2O_3, the standard enthalpy of formation was taken from [6]. The standard entropy was taken as the arithmetic mean of the data calculated by the methods in [2, 7–9]. For estimation of $H^\circ_{298}-H^\circ_0$ and $C_p=g(T)$, the methods used in [10] and [11], respectively, were applied.

The TM of the synthesis of Cu_2O_3 from the initial Cu(Cu_2O/CuO) and oxygen was performed for the system including condensed Cu, Cu_2O, CuO and Cu_2O_3, gaseous O_2, O and copper vapor at $P=10^5$ Pa and $T=100$–1200 K. The stability of Cu_2O_3 was studied in oxygen atmosphere at $P=0.1$–$1\cdot10^8$ Pa. The influence of the oxygen partial pressure on the stability of Cu_2O_3 was investigated at $P=10^5$ Pa and varying compositions of initial gas mixtures, ranging from pure oxygen to pure argon [12].

The essence of the ISIP model is given in [13]. In the present work, we used its simplest variant. The constituents of the solution were Y_2O_3, BaO, Cu_2O, CuO and Cu_2O_3. The compositions of the initial systems included condensed metals and oxides, gaseous oxides, O_2, O and metal vapor. The contents of each metal in the system corresponded to the ratios, characteristic of the particular superconductor under study.

The percentage Cu^{3+} content of the copper was calculated via the equation

$$[Cu^{3+}] = \left[\frac{n(Cu^{3+})}{n(Cu^{3+}) + n(Cu^{2+}) + n(Cu^{+})}\right]100 = \left[\frac{n(Cu^{3+})}{n(Cu)}\right]100 \qquad (1)$$

where $n(Cu^{1+})$ is the number of atoms of copper in the ± state, and $n(Cu)$ is the common number of copper atoms in each molecule of superconductor (solution).

TM was carried out in oxygen atmosphere ($P=10^5$ Pa) in the interval from 100 K to 1200 K in steps of 100 K.

Results and discussion

Properties and stability of Cu_2O_3 [12]

The main thermochemical properties of Cu_2O_3 are given in Table 1. The results of TM are presented in Figs 1–3.

Table 1 Thermochemical properties of Cu_2O_3

ΔH^o_{298} / kJ mol^{-1}	S^o_{298} / J (K mol)$^{-1}$	$H^o_{298}-H^o_O$ / J mol^{-1}	T_{decomp} / K	ΔH_{decomp} / kJ mol^{-1}	$C_p=a+b\cdot10^{-3}T-c\cdot10^5T^{-2}$/J (K mol)$^{-1}$		
					a	b	c
−335.0	100±11	16555	380	30.4	115.06	15.795	15.55

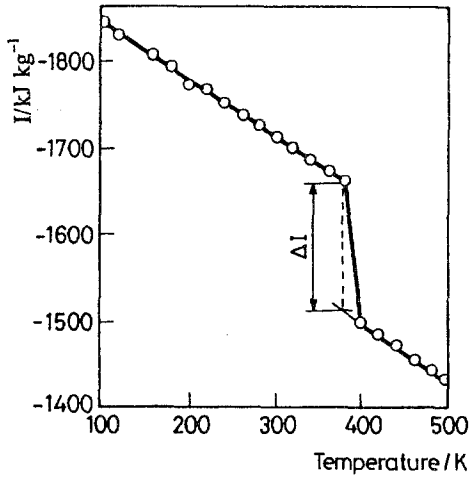

Fig. 1 Changes in full enthalpy (I) in initial system $Cu_2O_3 - O_2$ with elevation of temperature at $P=10^5$ Pa

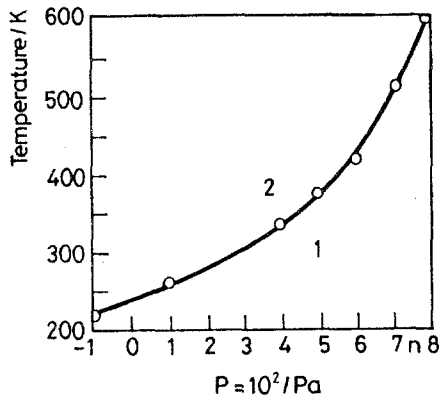

Fig. 2 Dependence of $T_{decomposition}$ of Cu_2O_3 on pressure in oxygen medium

It may be seen from Fig. 1 that changes in the full system enthalpy (ΔI) are observed at 380 K. This is connected with the phase transformation

$$Cu_2O_3(cr) \rightarrow 2CuO(cr) + 0.5O_2 \quad (2)$$

At higher temperatures, only CuO would exist. On increase of the oxygen pressure from 10^5 Pa to 10^8 Pa, the temperature of the phase transformation rises from 380 to 640 K. An oxygen pressure decrease from 10^5 to 0.1 Pa is accompanied by $T_{ph.tr}$ decreasing from 380 to 240 K (Fig. 2). From Fig. 3a, it is seen that, when $p(Ar)$ in the $Ar+O_2$ mixture is raised, the limit of existence of Cu_2O_3 moves to

lower temperatures. In initial Ar atmosphere ($P=10^5$ Pa), the molar content of CuO in the $CuO+Cu_2O_3$ mixture can be calculated from the equation

$$\log(X_{CuO}) = 8.6248 - 3.218 \cdot 10^3 \quad (1/T, K^{-1}) \tag{3}$$

At $T=380$ K and $P=10^5$ Pa, on increase of $p(O_2)$ in the system, the molar content of Cu_2O_3 in the phase mixture $CuO+Cu_2O_3$ also increases (Fig. 3b).

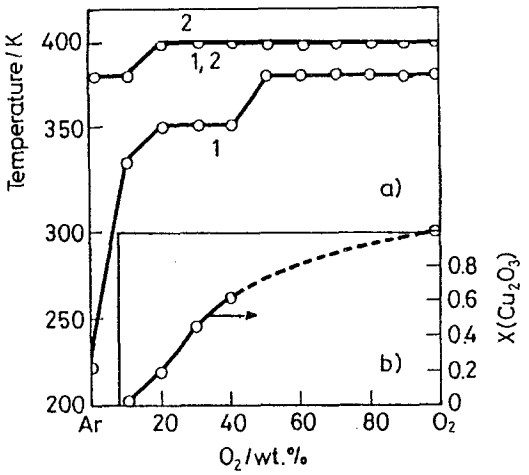

Fig. 3 Changes in range of temperature of existence of Cu_2O_3 (1), CuO (2) and their mixtures (1, 2) as a function of the oxygen partial pressure ($P_{common}=10^5$ Pa) (a). Dependence of mole fraction of Cu_2O_3 in the mixture Cu_2O_3+CuO on the oxygen partial pressure at 380 K and $P_{common}=10^5$ P (b)

The data show that crystalline Cu_2O_3 can exist as an individual phase. The majority of investigators (see, for example, [14–18]) have tended to accept that the Cu^{3+} state in the individual and double oxides is not stable under the usual conditions, and that high oxygen pressure must be used for the production of $LaCuO_3$ [16], $YCuO_3$ [17] and $LaSrCuO_4$ [18]. However, in the synthesis of the perovskite structure, stable Cu^{3+}–Cu^{2+} contents can be achieved at $P=10^5$ Pa in media of O_2/air, as a rule at $T\leq$400–500°C [19–22].

For individual Cu_2O_3, we have found only one known characteristic. According to [23], this oxide decomposes at 100°C (373 K). This agrees well with our data.

TM of solutions

The results are given in Table 2 and Figs 4–6.

It is seen from Table 2 that at $T<600$ K the content of Cu^+ is approximately equal to 0; at $T>600$ K, the Cu^+ content increases from $1 \cdot 10^{-6}$% (600 K) to 2.04–2.55% (1200 K). Consequently, for all solutions, only the Cu^{2+} and Cu^{3+} states of copper predominate.

Table 2 The contents of various valency states of copper in the model solutions in % from total amounts of copper in solutions

T/K	123-O_x			123.5-Oy			124-O_z		
	Cu^{1+}	Cu^{2+}	Cu^{3+}	Cu^{1+}	Cu^{2+}	Cu^{3+}	Cu^{1+}	Cu^{2+}	Cu^{3+}
100	0	$6.2 \cdot 10^{-5}$	100	0	$5.9 \cdot 10^{-5}$	100	0	$5.7 \cdot 10^{-5}$	100
200	0	0.805	99.19	0	0.768	99.23	0	0.74	99.26
300	0	17.2	82.8	0	16.51	83.49	0	15.96	84.04
400	0	60.08	39.92	0	58.71	41.29	0	57.6	42.4
500	0	87.54	12.46	0	86.83	13.17	0	86.24	13.76
600	$2 \cdot 10^{-6}$	95.6	4.33	$1.04 \cdot 10^{-6}$	95.39	4.607	$1.1 \cdot 10^{-6}$	95.16	4.84
700	$6.8 \cdot 10^{-5}$	98.08	1.00	$7.4 \cdot 10^{-5}$	97.96	2.04	$7.7 \cdot 10^{-5}$	97.85	2.15
800	$1.6 \cdot 10^{-3}$	98.97	1.09	$1.7 \cdot 10^{-3}$	98.9	1.095	$1.8 \cdot 10^{-3}$	98.84	1.15
900	$1.8 \cdot 10^{-2}$	99.4	0.6	$1.8 \cdot 10^{-2}$	99.3	0.673	$1.9 \cdot 10^{-2}$	99.7	0.71
1000	0.123	99.45	0.426	0.131	99.41	0.456	0.138	99.38	0.48
1100	0.578	99.12	0.308	0.617	99.05	0.329	0.651	98.87	0.346
1200	2.04	97.73	0.23	2.18	97.58	0.246	2.3	97.45	0.26

Table 2 Continued

T/K	125-O_q			126-Om		
	Cu^{1+}	Cu^{2+}	Cu^{3+}	Cu^{1+}	Cu^{2+}	Cu^{3+}
100	0	$6.4 \cdot 10^{-5}$	100	0	$1.8 \cdot 10^{-3}$	100
200	0	0.698	99.302	0	1.19	98.81
300	0	15.155	84.845	0	25.05	74.95
400	0	55.875	44.125	0	75.23	24.77
500	0	85.307	14.693	0	94.23	5.77
600	$1.2 \cdot 10^{-6}$	94.78	5.22	$4.2 \cdot 10^{-5}$	98.16	1.835
700	$8.4 \cdot 10^{-5}$	97.675	2.325	$2.9 \cdot 10^{-4}$	99.208	0.791
800	$1.9 \cdot 10^{-3}$	98.748	1.25	$6.7 \cdot 10^{-3}$	99.57	0.42
900	$2.2 \cdot 10^{-2}$	99.21	0.768	0.037	99.66	0.33
1000	0.15	99.33	0.52	0.506	99.32	0.172
1100	0.704	98.92	0.375	2.33	97.55	0.121
1200	2.55	97.24	0.28	7.68	92.23	0.085

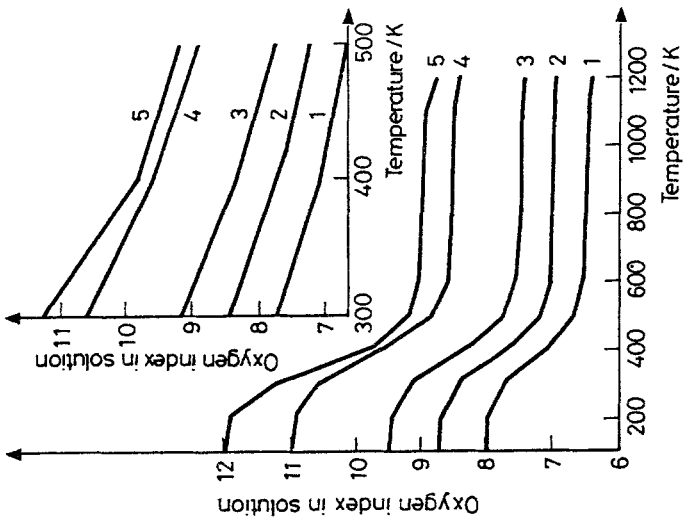

Fig. 5 Dependence of [oxygen index] *vs.* T in model solutions: 1: (123-O_x), 2: (123.5-O_y), 3: (124-O_z), 4: (125-O_q) and 5: (126-O_m)

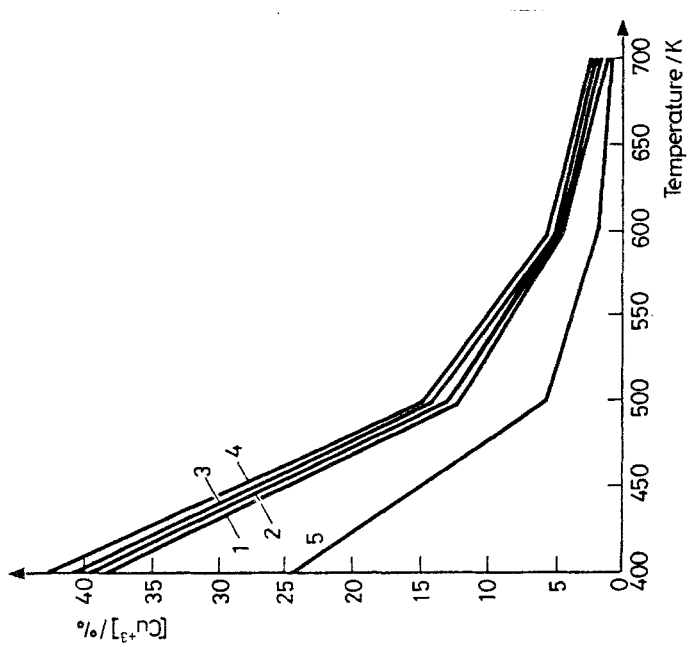

Fig. 4 Dependence [Cu^{3+} content] *vs.* T in model solutions: 1: (123-O_x), 2: (123.5-O_y), 3: (124-O_z), 4: (125-O_q) and 5: (126-O_m)

Table 2 and Fig. 4 reveal that, in the interval 200–500 K, the concentrations of Cu^{2+} and Cu^{3+} change very sharply: the Cu^{3+} content decreases and the Cu^{2+} content increases. This is connected with the thermal stability of the Cu^{3+} state in model solutions. The dependences of (x, y, z, q, m) *vs.* T (Fig. 5) show that the oxygen indexes decrease in the interval 100–1200 K, especially sharply at 200–500 K. This fully agrees with the changes in the Cu^{3+} contents in the solutions with temperature.

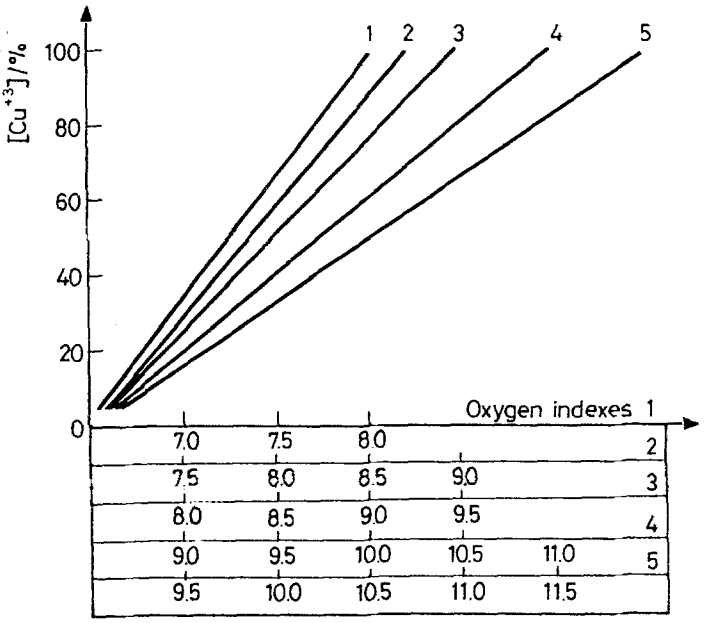

Fig. 6 Dependence of [Cu^{3+} content] *vs.* [oxygen index] in model solutions: 1: (123-O_x), 2: (123.5-O_y), 3: (124-O_z), 4: (125-O_q) and 5: (126-O_m)

The dependences of Cu^{3+} content *vs.* (x, y, z, q, m) are presented in Fig. 6. For every model solution, the Cu^{3+} content can be calculated via the following equations (in atomic percentage, from the common number of copper atoms in solution):

$$123\text{-}O_x: \quad [Cu^{3+}] \cong -433.866 + 66.71538x \tag{4}$$

$$123.5\text{-}O_y: \quad [Cu^{3+}] \cong -407.4806 + 58.1893y \tag{5}$$

$$124\text{-}O_z: \quad [Cu^{3+}] \cong -374.863 + 49.9708z \tag{6}$$

$$125\text{-}O_q: \quad [Cu^{3+}] \cong -341.3257 + 40.1467q \tag{7}$$

$$126\text{-}O_m: \quad [Cu^{3+}] \cong -299.985 + 33.3357m \tag{8}$$

Of course, direct comparisons of Cu^{3+} contents and oxygen indexes in real superconductors and ideal model solutions at the same temperatures would be incor-

rect: for the given initial conditions, the structure of superconductors/ideal model solutions must be different, as well as the properties connected with structure.

In order to be able to utilize the data obtained, we made the following suppositions:

i) The Cu^{3+} and Cu^{2+} contents in the YBaCuO superconductors/ideal solutions determine only the values of and changes in the oxygen index in a definite phase/solution. The number of oxygen atoms connected with Y and Ba is always constant.

ii) Under equilibrium conditions for superconductors, the ratios of Cu^{3+} and Cu^{2+} contents and oxygen indices can be found from data obtained in computer experiments with use of the ISIP model (Fig. 6, Eqs (4–8)).

Evaluation of some properties for superconductors

The connection between the values of ΔH°_{298} for HTSC and solution for every family of HTSC/solution at equivalent meaning of the oxygen indexes (x, y, z, q, m) was determined in the following way.

It is known that for complex oxides

$$\Delta H^{\circ}_{298}(el)_j = \sum n_i \Delta H^{\circ}_{298}(i) + \Delta H^{\circ}_{298}(ox)_j \tag{9}$$

where $\Delta H^{\circ}_{298}(el)_j$ and $\Delta H^{\circ}_{298}(ox)_j$ are the standard enthalpies for the elements and simple oxides, respectively; n_i is the number of moles of the simple i-th oxide in the complex, and $\Delta H^{\circ}_{298}(i)$ is the standard enthalpy of the i-th oxide.

Taken into account the information obtained from the computer investigation of solid solutions, we made the supposition that

$$\Delta H^{\circ}_{298}(el)_j \cong \sum n_i^{sol} \Delta H^{\circ}_{298}(i) + \Delta H^{\circ\,sol}_{298}(ox)_j \tag{10}$$

where sol relates to solution, and n_i^{sol} is the number of moles of the i-th simple oxide in solution.

In principle:

$$\sum n_i \Delta H^{\circ}_{298}(i) \neq \sum n_i^{sol} \Delta H^{\circ}_{298}(i) \quad \text{and} \quad \Delta H^{\circ}(ox)_j \neq \Delta H^{\circ\,sol}_{298}(ox)_j \tag{11}$$

as Cu_2O_3 was used for the first time as a constituent of the solution, and n_i^{sol} were determined in the modeling, but not as the ratios of the simple oxides in the HTSC molecule.

For known oxygen indexes (x, y, z, p, q), the numbers of Cu_2O_3 and CuO moles in solutions were calculated with the help of the following equations:

$$n^{sol}_{Cu_2O} = ([Cu^{3+} \text{ in } \%]n_{Cu})/200 = [\{A+B(x,y,z,q,m)\}n_{Cu}]/200 \tag{12}$$

$$n^{sol}_{CuO} = n_{Cu} - ([Cu^{3+} \text{ in } \%]n_{Cu})/100 = n_{Cu} - [\{A+B(x,y,z,q,m)\}n_{Cu}]/100 \tag{13}$$

where n_{Cu} is the common number of copper atoms in the HTSC molecule; $[Cu^{3+}]$ is calculated by means of Eqs (4)–(8).

For the stable oxides Y_2O_3 and BaO:

$$n^{sol}_{Y_2O_3} = n_{Y_2O_3} \text{ and } n^{sol}_{BaO} = n_{BaO} \tag{14}$$

The most important problem is the determination of $\Delta H^{sol}_{298}(ox)$. Analysis of the data obtained, and their comparison with literature data [24] show that, for all types of HTSC and oxygen indices values

$$\Delta H^{sol}_{298}(ox)_j \cong n^{sol}_{Cu_2O_3} \Delta H^{o}_{298}(Cu_2O_3) \tag{15}$$

Thus, the full equation for calculation of $\Delta H^{o}_{298}(el)$ for every HTSC in the system YBaCuO is

$$\Delta H^{o}_{298}(el)_j = n^{sol}_{Y_2O_3} \Delta H^{o}_{298}(Y_2O_3) +$$

$$+ n^{sol}_{BaO} \Delta H^{o}_{298}(BaO) + n^{sol}_{CuO} \Delta H^{o}_{298}(CuO) + 2n^{sol}_{Cu_2O_3} \Delta H^{o}_{298}(Cu_2O_3) \tag{16}$$

The standard enthalpies of HTSC calculated with the help of (16) differ from the literature data within limits of ±1.5% (Table 3).

The energetic 'addition' (15) permits creation from the ISIP structure of the perovskite type structure of the complex copper-containing oxide. As this 'addition' for all HTSC is connected with $n^{sol}_{Cu_2O_3}$ and $\Delta H^{o}_{298}(Cu_2O_3)$, it is possible to assume that the creation of superconducting structures is mainly connected with definite energetic expenditures for the distribution of Cu^{3+} (and connected oxygen ions) in definite positions of the crystalline lattices.

As $\Delta H^{sol}_{298}(ox)$ is always negative, the structures of HTSC are more thermodynamically stable than the solid solution structures with the same compositions.

The additive properties $S^{o}_{298}(j)$ and $C^{o}_{p298}(j)$ were calculated with the help of the following equations:

$$S^{o}_{298}(j) \cong \sum n^{sol}_i S^{o}_{298}(i) = n^{sol}_{Y_2O_3} S^{o}_{298}(Y_2O_3) + n^{sol}_{BaO} S^{o}_{298}(BaO) +$$

$$+ n^{sol}_{CuO} S^{o}_{298}(CuO) + n^{sol}_{Cu_2O_3} S^{o}_{298}(Cu_2O_3), \tag{17}$$

$$C^{o}_{p298}(j) \cong \sum n^{sol}_i C^{o}_{p298}(i) = n^{sol}_{Y_2O_3} C^{o}_{p298}(Y_2O_3) + n^{sol}_{BaO} C^{o}_{p298}(BaO) +$$

$$+ n^{sol}_{CuO} C^{o}_{p298}(CuO) + n^{sol}_{Cu_2O_3} C^{o}_{p298}(Cu_2O_3). \tag{18}$$

The results of calculating with Eqs (17) and (18) differ from the literature data within ±1.2% (Table 3). All data for simple oxides are taken from [12, 24].

Table 3 The results of comparison between the known and calculated properties values of superconductors in the Y–Ba–Cu–O system

Supercon-	ΔH°_{298} /kJ mol^{-1}		δ/	S°_{298} /J (K mol)$^{-1}$		δ/	C°_{p298} /J (K mol)$^{-1}$		δ/
ductor	$Data_{Lit}$	Calc.	%	$Data_{Lit}$	Calc.	%	$Data_{Lit}$	Calc.	%
123-O_7	–2706 [26]	–2748	–1.5	323.1 [27]	324.7	+0.5	283.7 [27]	281.5	–0.8
				321.7 [29]		+0.9			
123.5-$O_{7.5}$	–2794 [26]	–2850	–2.0	345.1 [27]	350.8	+1.6	305.5 [27]	308.6	+1.0
124-O_8	–2881 [26]	–2928	–1.6	367.2 [27]	370.7	+1.0	322.5 [27]	329.7	+2.2
125-O_9	–3055 [26]	–3082	–0.9	411.4 [27]	408.6	–0.7	372.6 [27]	369.7	–0.8
123-$O_{6.65}$	–2677 [28]	–2600	+2.9	–	–	–	–	–	–
123-$O_{6.69}$	–2689 [28]	–2665	–0.9	323.7 [30]	326.0	+0.9	–	–	–
123-$O_{6.93}$	–2713 [28]	–2742	–1.0	–	–	–	–	–	–
123-$O_{6.9}$	–	–	–	319.9 [31]	330.2	+3.2	–	–	–
123-$O_{6.85}$	–	–	–	323.5 [30]	323.6	+0.03	–	–	–
			$\bar{\delta} = \pm 1.5$			$\bar{\delta} = \pm 1.1$			$\bar{\delta} = \pm 1.2$

It is seen that the methods developed for determination of the most important thermochemical properties of the HTSC yield satisfactorily correct data.

Possible connection between T_c and Cu^{3+} content for superconductors (Fig. 7)

This dependence involved application of the mean T_c values of some superconductors (Table 4) and the Cu^{3+} contents obtained from the dependences oxygen index *vs.* Cu^{3+} content (Fig. 6, Eqs (4–8)). Figure 7 demonstrates a practically linear dependence

$$T_c(\text{in K}) \approx 45.32265 + 1.4333[Cu^{3+}(\text{in \%})] \quad (19)$$

This means that, for superconductors in the system YBaCuO, mainly the Cu^{3+}–Cu^{2+} contents determine the T_c values.

From Eq. (14) and Eqs (4–8), it is possible to evaluate T_c if the oxygen index of the superconductor is known; likewise, the oxygen index of the complex oxide can be estimated if the T_c value is known.

Thus, for 125-O_q T_c would be equal to 74 K, and for 126-O_m (T_c=55 K [32, 39]) the oxygen index m would be equal to 9.2.

Table 4 The oxygen indexes and T_c-values for superconductors in the YBaCuO system*

Superconductor	T_c/K	References
123-O_7	93	[25]
	92	[32]
123-O_7	$\overline{T}_c$=92.0 K	
124-$O_{7.85-8.1}$	80	[33]
	80.4	[32]
	79	[34]
	81	[35]
124-O_8	$\overline{T}_c$=80 K	
123.5-$O_{7.15-7.5}$	14-68**	[36]
	86	[37]
	70	[32]
123.5-$O_{7.25}$	$\overline{T}_c$=70 K	
125-O_9	–	[38]
126-O_m***	$\overline{T}_c$=55	[32, 39, 40]
123-$O_{6.8}$	$\overline{T}_c$=76	[40–47]
123-$O_{6.6}$	$\overline{T}_c$=52	[40–47]

* the majority of data taken from [25];

** do not taken into accunt T_c values of HTSC synthesized at high oxygen pressures;

*** this phase can found as impurity.

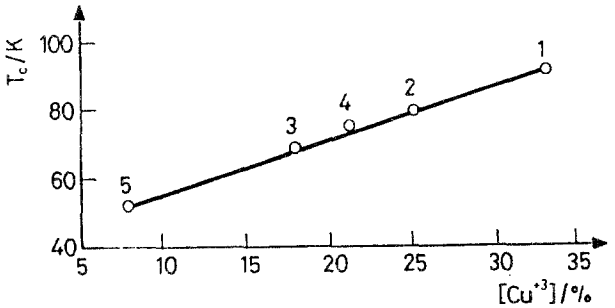

Fig. 7 Dependence of T_c *vs.* [Cu^{3+} content] for some superconducting phases in the system YBaCuO: 1: (123-O_7), 2: (124-O_8), 3: (123.5-$O_{7.25}$), 4: (123-$O_{6.8}$) and 5: (123-$O_{6.6}$)

Conclusions

Theoretically, it has been shown that the hypothetical oxide Cu_2O_3 can exist as an individual phase at low temperatures. It would be desirable to confirm this experimentally, to verify the main thermochemical properties and to investigate the structure parameters for Cu_2O_3.

For superconductor families in the system YBaCuO, use of the calculated thermodynamic functions of Cu_2O_3, the model of ideal solution of interaction products, thermodynamic simulation methods and some suppositions has shown that the Cu^{3+}–Cu^{2+} contents are the dominating factors for every superconductor; this permits determination of the common oxygen index in the formula and some equilibrium properties.

For complex superconducting cupper-containing oxides, a procedure for evaluation of some thermochemical properties is suggested.

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