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SOME THERMODYNAMIC ASPECTS OF HIGH T_c SUPERCONDUCTORS

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Abstract

Thermochemical and thermodynamical properties of HTSC phases are reviewed for the Y–Ba–Cu–O system and also presented for the newly calculated Bi–Sr–Cu–O system stressing out stoichiometric and phenomenological viewpoints. Simulated data are listed for $(H^o_{298}-H^o_0)$, phase transformation temperatures, standard entropies, standard enthalpies of formation, heat capacities in crystalline phase, etc. Pseudobinary phase diagrams are treated showing the effect of oxygen partial pressure particularly illustrated on the (Sr, Bi, Ba)–Cu–O system.

Keywords: data simulation, enthalpy, non-stoichiometry, oxide superconductors, phase diagrams, thermodynamics, Y–Ba–Cu–O and Bi–Sr–Cu–O systems

Introduction

No other field has attracted so much attention and publication activity than that of oxide high temperature superconductors (HTSC). Beside the specific journals exclusively devoted to this topic (e.g. Physica C, Supercond. Res. and Tech.) the other journal have also used the opportunity to include HTSC papers sometime publishing whole volumes as monothematic monographs, e.g., Thermochimica Acta 1991 [1]. One of the most important and attractive problems are caloric and thermochemical properties where the thermodynamic stability of HTSC associated substances plays a major role. It can be solved by means of thermodynamic investigations including experimental studies as well as theoretical calculations which require a vast amount of data. There are various methods of thermodynamic estimation which provide a feasible and valuable tool of the simulation and extrapolation of thermodynamic data to the range of variables where experimental data are lacking. When using the term thermodynamic "equilibrium" the stability aspect with respect to stable and metastable systems and phases must be considered [2]. There are different wellknown approaches to obtain the temperature, pressure and composition of a multicomponent system at equilibrium in order to study an appropriate

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phase diagrams. The obvious method is a purely experimental one, this is for instance, a direct measurement of phase composition at equilibrium when temperature, pressure and other intensive parameters are defined. Several experiments with different temperatures seem to be a way how to obtain a phase diagram of a system under investigation although such direct experimental studies are laborious and time-consuming moreover bearing a most severe problem how to attain a true equilibrium. Therefore both stable and metastable phase boundaries are simultaneously observed [2] further complicated by oxygen stoichiometry because of a free exchange of this volatile component with environment. The most widely investigated system is that of Y–Ba–Cu–O [3] (YBCO) where three superconductors from the family of phases $Y_2Ba_4Cu_{6+n}O_{14+\delta}$ (with $n = 0$, 1 and 2) have already been obtained in various forms including bulk crystals. Unfortunately, only a little portion of reports have been directed to study the thermodynamic properties of HTSC phases which is true even for the YBCO system although a self-consistent set of thermodynamic functions was already published by several authors but has to be continued in order to become generally useful. All these aspect will be the main objects of our discussion below stressing out particularly our preceeding investigations.

Our previous studies on the $YBa_2Cu_3O_\delta$ related phases

In the early years 1988–92 we got successfully engaged in studying phase diagrams in the YBCO system [4–12] and succeeded to investigate the pseudobinary cut of $YCuO_{2.5}$–$YBa_2Cu_3O_{6.5}$–$BaCuO_2$ and the characteristics of $YBa_2Cu_3O_{6.5}$ phase [4]. An improved experimental determination of oxide phase equilibria was proposed being based on the separation of the melt from an equilibrated sample by soaking melt into the supportiong Y_2O_3 pellet and the consequent analysis of its solid residual [5]. This method has been applied to growing single crystals [6]. It matured to several review articles [8–15] and consequent attempt to prepare YBCO doped polycrystalline materials through fast melt solidification and glass recrystallization [15–18]. Since 1992 we moved to studying thermodynamics, first simulating the YBCO deposition from vapor/gas [19] followed by thermodynamic and structural considerations on compatibility of various substrates for the YBCO thin film formation [20]. Thermodynamical and thermochemical estimation and calculations methods have been in the center of our interest until now [24–35].

It was shown, for example, that thermodynamic simulation of the $YBa_2Cu_3O_\delta$ (123_δ, $\delta \geq \delta \leq 7$) formation [21] can be realised on basis of a formal mixing of the end members, i.e. both 123 phases having the oxygen content 6 and 7. To find the enthalpies of mixing, ΔH_{mix}, the known values of formation enthalpies, H^o_{298}, have to be employed from literature, e.g., using less recent series [22]:

δ =	6	6.25	6.47	6.5	6.69	6.93	7	
ΔH^o_{298} =	2630	2671	2672	2677	2689	2713	2772	kJ mol^{-1}

and fitted by a polynomial to match either ideal, regular (all data upper raw 1 or selected data lower raw 2) or subregular solid solution models. The coefficients of the polynomial $\Delta H^{\circ}_{298}=a+b\delta+c\delta^2+d\delta^3$ and the end values of the individual models are as follows:

Model	Coefficient				$-\Delta H^{\circ}_{298}$		Corr. coeff.	Deviation
	a	b	c	d	$\delta=6$	$\delta=7$		
Ideal	–2641	–76.8			2642	2718	0.856	0
1-regular	–2634	–124.5	45.7		2680	2733	0.866	+
2-regular	–2680	–64.7	–109		2642	2718	0.923	+
Subregular	–2631	–220.5	316	–181.5	2631	2717	0.864	–

The best fit provides seemingly the regular model of solid solution with a positive deviation from the linear interpolation of given experimental data. The character of the cubic dependence allows one to estimate the heat of mixing from the symmetrical dependence according to:

Regular (1): $-57.7\ \delta^2$ with ΔH_{mix} at $\beta=0.5$ equal 14.5 kJ mol^{-1}

Regular (2): $107.7\ \delta^2$ with ΔH_{mix} at $\beta=0.5$ equal 26.9 kJ mol^{-1}

On the other hand the change of the oxygen stoichiometry can be viewed as a series of superstructures with characteristic values of δ following the number of fully occupied oxygen chains, e.g., non (deoxygenated-tetra, $\delta=6$), every two in five ($\delta=6.65$), every second chain ($\delta=6.85$), and all (oxygenated-tetra, $\delta=7$) [23].

Thermodynamics, stoichiometry and stability

It was found that the actual formulae of HTSC are sensitive to experimental conditions and can be strongly dependent not only on the overall, but also local, energetic state [12]. Possible sources for such stoichiometric changes can be either the action of the external force fields or the effect of the internal make-up. The excess of surface energy of very thin layers enveloping grains results from a very high curvature of extremelly small particles or from pressure contacts between the grains created in well-compacted samples. Similarly a structural misfit of thin HTSC layers deposited on various substrates [20] can produce strain or the strain sites can be created during the formation of off-stoichiometry inclusions with the dimension near lattice parameters. Another source of stoichiometric changes can be located on the boundary of currents passing the crystal lattice or in the vicinity of negative electrodes [34]. In contradiction to structural models we can hypothetically account for the existence of various phases yet unknown by a formal extending the cation ratios to ranges of yet undetermined compounds which is well compatible with our

Table 1 Hypothetical changes of ratios (Y+Ba):Cu=⊗

Composition shift	$Y_1Ba_2Cu_3O_\delta$ supercond. phase		$Y_1Ba_3Cu_2O_\delta$		$Y_2Ba_1Cu_1O_\delta$ "green" phase	
	Y:Ba:Cu	⊗<1	Y:Ba:Cu	⊗≅2	Y:Ba:Cu	⊗>2.5
Basic formulae	1 2 3	1	1 3 2	2	2 1 1	3
Exchange of Y⇔Ba	1 1 2	1	1 5 3	2	1 2 1	3
Multiplication of (Y+Ba)	(1 3 3)	–	3 8 5	2.2	1 3 1	4
	(2 2 3)	–	1 6 3	2.4	2 2 1	4
Multiplication of (Cu)	2 4 7	0.9	1 3 3	1.3	(2 1 2)	–
	1 2 4	0.7	2 2 3	1.3	(2 1 3)	–
	1 2 5	0.6				
Unequal change (Y⇔Ba⇔Cu)	2 3 5	1	1 4 3	1.7	2 3 2	2.5
	4 1 5	1	2 1 2	1.5	1 4 2	2.5
	1 3 5	0.8	1 2 2	1.5	(1 3 2)	–

sources of the stoichiometry changes accounted for $Y_1Ba_2Cu_3O_\delta$:

oxygen (δ)	cations ratios (Y:Ba:Cu)
stress sites	high curvature, interfaces
surface layer	(Y–Ba) (Cu)
(tetra-ortho)	vicinity of charge, supercurrents
valence changes	(Y–Ba–Cu)
impurities	metastability due to freeze-in, inclusions
dopants (*M*)	(Y–Ba)–M

phenomenological thermodynamic calculations. Accordingly, the extent of possible variations of the cation ratios can be formally derived using the schema shown in Table 1, where we can phenomenologically assume the change of cation stoichiometry in three groups and four gradual levels regardless to real structures [24]. For most of the existing and derived compounds their thermodynamic and thermochemical properties were not found to be determinable by conventional estimations and thus our calculations using special empirical and quasi-thermodynamical methods and computer programs [31, 35] became a useful tool.

Simulation of thermodynamic and thermochemical data

We already published reviews and refinements of the known and estimated thermochemical properties such as metastability [25], $(H^0_{298}-H^0_0)$ and the phase transfor-

Table 2 Thermochemical and thermodynamical properties of some compounds in the Y–Ba–Cu–O system

Oxide	ΔH^{o}_{298} / kJ mol^{-1}	S^{o}_{298} / J K^{-1} mol^{-1}	$H^{o}_{298}-H^{o}_{o}$ / J mol^{-1}	$c_p=a+b\times10^{-3}T-c\times10^{5}T^{-2}$/ J K^{-1} mol^{-1}			$T_{ph.tr}$/ °C	$\Delta H_{ph.tr}$/ J mol^{-1}	$c_{p,ph.tr}$/ J K^{-1} mol^{-1}
				a	*b*	*c*			
123-O6	–2586.8±7.9	319.86	49352	307.48	76.28	26.213	1373	1370	362.12
123-O7	–2706.3±2.4	323.06	51107	315.29	54.47	42.450	1288	110900	418.10
123.5-O7.5	–2794.5±3.5	345.15	54040	305.12	84.56	22.064	1190	23400	416.60
124-O8	–2881.2±5.7	367.24	57750	356.72	45.74	42.470	1110	9200	445.80
125-O9	–3055.2±10.5	411.42	65610	363.27	114.67	22.064	1023	8900	498.20
143-O8.5	–3828.3±14.2	454.15	70016	312.96	41.07	42.810	1170	156500	357.90
211-O5	–2712.0±2.6	223.00	35344	206.10	35.20	20.925	1543	31200	262.00
$YCuO_2$	–1038.6±24.3	98.81	15677	92.90	16.36	8.050	1843	64500	125.60
$Y_2Cu_2O_5$	–2214.8±5.1	200.83	31360	201.65	41.85	18.155	1428	1430	265.14
Y_2BaO_4	–2533.5±0.7	178.81	28128	164.65	20.53	20.320	1673	9800	198.37
$Y_2Ba_2O_5$	–3131.0±6.4	245.16	37905	227.88	22.05	36.734	1313	10200	249.27
$Y_2Ba_4O_7$	–4314.1±7.5	377.84	57346	335.28	24.60	52.440	1413	28100	386.75
$Y_4Ba_3O_9$	–5666.6±9.3	424.00	66049	393.75	48.23	44.915	2433	245700	510.18
$BaCuO_2$	–782.0±21.4	110.52	17020	91.45	24.42	7.245	1318	28300	122.46
$BaCu_2O_2$	–807.0±7.4	151.51	22707	118.30	27.09	8.010	1500	42800	163.76
Ba_2CuO_3	–1409.1±29	176.87	26730	145.32	28.77	16.594	1123	4300	176.00
$BaCu_5O_8$	–2656.4±4.9	420.00	65590	354.18	113.42	24.90	1073	3100	445.05

mation temperatures [26], standard entropies of formation [27], heat capacities in crystalline phase [28], heats of melting/decomposition [29] and average heat capacities of phases transformation products [30]. The multitude of literature data on properties of complex oxides, their critical analysis and calculation, and also the statistical methods used for the determining reliable data were also described in detail [26–33] and the final thermochemical properties of the complex oxides are given in Table 2.

Standard enthalpies of formation

On the basis of above mentioned treatments [31–35] we analysed available sources and data priority accounting for [33] :

- Repeated or close values reported by different researches using various experimental techniques,
- Results published by representative laboratories,
- Most recent papers and
- Neglection of extreme values.

Consequently we treated averaged data of 11 characteristic YBCO compounds in order :

- to find some regularities in the published values,
- to try the derivation of certain empirical dependences and
- to estimate the extrapolated data of related compounds difficult to measure and/or to exist only hypothetically.

One of the most important characteristics is the standard enthalpy of formation, $\Delta_f H^0_{298}(j)$, which can be presented in the following way:

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

where m_i and $\Delta H^0_{298}(i)$ are the number of moles and the standard enthalpy of formation of the i-th simple oxide of the j-th complex, respectively and $\Delta H^0_{298}(ox)_j$ is the standard enthalpy of formation of the j-th complex from simple ones. As a result the empirical dependences based on the number, m, of oxygen atoms in the molecule of a compound in question [24] were employed in the three gradual manners. First using a simple relation of $\Delta_f H^0_{298}(ox)_j$ equal to (am) and to $(a+bm)$ and then a more complex average method of the five simultaneously applied equations for

$$\Delta H^0_{298}(ox)_j = a+bm, \ = a+b\Sigma N, \ = a+b\ln\Sigma N, \ = a+b\Sigma M \text{ and } = a+b\ln\Sigma M,$$

where ΣN is the sum of number of elements in a molecule and ΣM is the molecular mass of a compound. The resulting data of individual treatments are compared in Table 3 [33].

Table 3 Standard enthalpies of formation from simple oxides

Compound	$-\Delta_f H^0_{298}(ox)$/kJ mol^{-1}			
	Equation employed:			
	literature data	$-29.274xm$	$13.3-14.5xm$ $235.3-51.6xm$	average method (⊕)
$BaCuO_2$	73.4∓21.4	59.5	–	73.4∓21.4
Ba_2CuO_3	108∓29	89.2	–	108∓29
Y_2BaO_4	73∓40	119.0	44.7	61.2∓0.7
$Y_4Ba_3O_9$	224.3∓145	267.7	229.1	184.8∓9.3
Y_2BaCuO_5	76.4∓36.4	148.7	59.2	84.6∓2.6
$YBa_2Cu_3O_6$	110.7∓54.5	178.4	74.3	126.6∓7.9
$YBa_2Cu_3O_7$	129.7∓14.3	208.2	125.9	134.2∓2.4
$YBa_2Cu_4O_8$	173.6∓46.4	237.9	177.5	154.0∓5.7
$YBa_4Cu_3O_{8.5}$	241.0∓11.2	252.8	151.7	190.2∓14.2
M⇒$Y_2Cu_2O_5$	-14.5∓5.1	148.7	59.2	-14.5∓5.1⇐M
$YCuO_2$	11.3∓15.6	59.5	15.7	4.5∓24.3
$YBa_2Cu_3O_{6.5}$	–	193.3	100.1	130.8∓3.3
$YBa_2Cu_{3.5}O_{7.5}$	–	223.0	151.7	144.6∓3.5
$YBa_2Cu_6O_9$	–	267.7	229.1	172.7∓10.5
Ba_3CuO_4	–	119.0	44.7	138.7∓6.4
$Ba_3Cu_5O_8$	–	237.9	177.5	210.9∓5.9
$Ba_2Cu_3O_5$	–	148.7	59.2	147.7∓18.5
$Y_2Ba_2O_5$	–	148.7	59.2	97.6∓6.4
$Y_2Ba_4O_7$	–	208.2	125.9	169.1∓7.5
$BaCu_2O_2$	38.2∓26.6	59.5	–	30.1∓12.4

y-containing	(⊕)	y-not containing (Ba)
$31.75-0.56\ \Sigma N$		$-18.166-0.547\ \Sigma N$
$603.72-129.94\ \ln\Sigma N$		$255.57-71.283\ \ln\Sigma N$
$32.86-0.25\ \Sigma M$		$-20.25-0.228\ \Sigma M$
$718.76-131.32\ \ln\Sigma M$		$303.58-69.17\ \ln\Sigma M$
$40.02-25.45\ m$		$-3.4-35\ m$

m – number of oxygen atoms in molecule, ΣN – sum of the number of elements in molecule, ΣM – sum of molecular mass of a compound, M⇒ – metastable.

Effect of the multiplication of oxide layers

The values of formation enthalpy can be consequently used to extract their partial values along the homological series. For example, according to the stoichiometry changes: $123_7 \rightarrow 124_8 \rightarrow 125_9 \rightarrow 1/2\ 247_{15}$ we can write following equations:

$$\Delta_f H^0_{ox}(298)(124_8) = \Delta_f H^0_{ox}(298)(123_7) + \Delta H(\mathrm{CuO}) \tag{2}$$

$$\Delta_f H^0_{ox}(298)(125_9) = \Delta_f H^0_{ox}(298)(123_7) + 2\Delta H(\mathrm{CuO}) \tag{3}$$

$$\Delta_f H^0_{ox}(298)(247_{15}) = 2\Delta_f H^0_{ox}(298)(123_7) + \Delta H(\mathrm{CuO}) \tag{4}$$

2x123_7		123_7		247_{15}	124_8		125_9	
–268.4		–134.2		–289.2	–154.0		–173.0	
	–20.8					–19.8		
			19.8		1/2 39.6			⇒ΔH(CuO)

The resulting value of the formation enthalpy of adding a single CuO is 19.8 kJ $\mathrm{mol^{-1}}$. Similarly we can estimate the value for $\mathrm{Cu_2O}$ assuming

$(011)\mathrm{BaCuO_2} = \mathrm{BaO+CuO}$; $(012)\mathrm{BaCu_2O_2} = \mathrm{BaO+Cu_2O}$;
–73.4 –86.4 $\Rightarrow \Delta H = -13$

which is in accordance with the estimate CuO(–155.15) – $\mathrm{Cu_2O}$(–167.28) = –12.13 kJ $\mathrm{mol^{-1}}$.

Accordingly we can calculate the multiplication of BaO layers assuming:

$$\Delta_f H^0_{ox}(298)(220_5) = \Delta_f H^0_{ox}(298)(210_4) + \Delta H(\mathrm{BaO}) \tag{5}$$

$$\Delta_f H^0_{ox}(298)(240_7) = \Delta_f H^0_{ox}(298)(210_4) + 3\Delta H(\mathrm{BaO}) \tag{6}$$

210		220		240		
–73		–97.6		–169.1		
	–24.6		–71.5		–32	⇒ΔH(BaO)

and

$$\Delta_f H^0_{ox}(298)(143_{8.5}) = \Delta_f H^0_{ox}(298)(123_{6.5}) + 2\Delta H(\mathrm{BaO}) \tag{7}$$

143	123		
–190.2	–130.8	–29.4	⇒ΔH(BaO)

Phase diagrams and oxygen partial pressure

Most of the phases in the systems in which the HTSCs have been observed [12–14], contain copper or oxygen in variable oxidation state. This variation of valency can be achieved either by substitution of some heterovalent cations or by modification of oxygen stoichiometry. As a rule, the oxygen content can be varied in some extent by adjusting the state of the surrounding atmosphere. There are two variables which influence the oxygen concentration in a condensed phase [36, 37] – temperature and partial pressure of oxygen in the atmosphere.

The variable oxygen content must be taken into account when a thermodynamic model of a given phase is constructed. At normal conditions, i.e. when temperature and pressure are adjustable parameters, the construction of thermodynamic model means to propose the form of Gibbs free energy as a function of these two parameters and chemical composition. If oxygen is a free component the Gibbs energy is to be recalculated with respect to its activity. For this reason it is convenient to introduce another thermodynamic potential (sometimes called hyperfree energy) [37]

$$Z = G - n_0\mu_0 \tag{10}$$

where G is Gibbs energy and n_0 and μ_0 are, respectively the molar quantity and chemical potential of oxygen. For such partially open system the chemical equilibrium is described by analogical relations as for closed system, except that G is replaced by Z. For instance, the well known equation for equilibrium between a solid phase and high temperature melt transforms to

$$\frac{\partial Z_q(l)}{\partial Y_{c_1}(l)} = \frac{Z_q(s) - Z_q(l)}{Y_{c_1}(s) - Y_{c_1}(l)} \tag{11}$$

where l and s stand for liquid and solid, respectively, Z_q are quasimolar hyperfree energies and Y_{c_1} is quasimolar fraction of stable component c_1. The term "quasi" means the quantity related to the sum of conservative components.

The thermodynamic models usually contain some free parameters which should be evaluated before they are applicable for the phase diagrams calculations. The equilibrium conditions like (Eq. (11)) can be used to refine the model parameters by fitting them on the experimental data. For the pseudobinary systems (with two conservative components) the usually available experimental data are from DTA measurements which provide the temperatures and compositions of eutectic and peritectic points at various values of P_{O_2}. For more complicated systems additional complementary methods (e.g. soaking method [5]) have to be applied.

Recently three pseudobinary systems – Sr–Cu–O, Bi–Cu–O and Ba–Cu–O – have been extensively studied [39] by the approach described above. The common component in all of them is copper and it was this particular component which was supposed to be responsible for variable oxygen concentration in the high temperature melt, while the other stable components were considered to bind the amount of oxygen corresponding to their standard valence states (Sr^{2+}, Ba^{2+}, Bi^{3+}). Consequently the thermodynamic behavior of CuO_x melt was of particular interest.

Particular case of CuO_x-based subsystems

Melt of CuO_x

The quasimolar hyperfree energy of the liquid phase CuO_x was modelled by the integral of its total differential [37]

$$Z_q^{(l)}(T,P_{O_2}) = Z_q^{(l)}(T^*,P_{O_2}^*) - \int_{T^*}^{T}(S_q(T) - 1/2\eta_O S_{O_2}(T))\mathrm{d}T -$$

$$- 1/2\ R\ln(P_{O_2})\int_{T^*}^{T}\eta_O(T,P_{O_2})\mathrm{d}T - 1/2\ RT\int_{P_{O_2}^*}^{P_{O_2}}\eta_O(T,P_{O_2})\mathrm{d}\ln(P_{O_2}) \qquad (12)$$

For the starting point of integration the equality of quasimolar hyperfree energies of $CuO(s)$, $Cu_2O(s)$ and $CuO_x(l)$ at the eutectic point ($T^*=1353$ K, $P_{O_2}^*=0.531$ [36]) was employed. The definite value was calculated using tabular data [38]. The oxygen concentration in the melt was described by empirical relation.

$$\eta_O(T,P_{O_2}) = 1 - (T - Q)^{1/2}\,(a - b(P_{O_2})^{1/3} \qquad (13)$$

which fits very well the experimental dependence found by Roberts and Smyth [36] in a broad range of partial pressure and temperature. The temperature dependence of quasimolar entropy was well described by simple relation

$$S_q(T) = E + F\ln(T) \qquad (14)$$

while the function $S_{O_2}(T)$ was taken from thermodynamic tables. All free parameters of the model (Q, a, b, E and F) were evaluated by the regression using the data taken from Ref. [36].

Pseudobinaries M–Cu–O (M=Sr, Bi, Ba)

For intermediary phases $M_{1-y}Cu_yO_\delta(s)$ (M=Sr, Bi, Ba) a simple model supposing the oxygen content being independent on both T and P_{O_2} was used. In such case the hyperfree energy

$$Z_q(T,P_{O_2}) = Y_{Cu}Z_q(CuO) + (1-Y_{Cu})Z_q(MO_\gamma) +$$

$$+ A + BT + CT\ln(T) - 1/2\ \Delta\eta_O RT\ln(P_{O_2}) \qquad (15)$$

is constructed as a weighted sum of contributions of respective oxides forming the given phase and the temperature dependence of the Gibbs energy of formation. The last term reflects the difference between the quasimolar fraction of oxygen in the intermediary phase and in the assembly of original oxides. For all considered solid phases excepting $Sr_{14}Cu_{24}O_{41}$ the coefficient $\Delta\eta_O$ which reflects this difference was regarded as zero.

The thermodynamic model for the mixed oxide melt of type $M_{1-y}Cu_yO_\delta(l)$ (M=Sr, Bi, Ba) is based on the assumption of mixing the $CuO_x^{(l)}$ liquid phase discussed above and the other part of the melt ($MO_\gamma^{(l)}$) with fixed oxygen content:

$$Z_q^{(l)}(T,Y_{Cu}) = Y_{Cu}Z_q(CuO_x^{(l)}) + (1 - Y_{Cu})Z_q(MO_\gamma^{(l)}) +$$

$$+ RT\left[Y_{Cu}\ln(Y_{Cu}) + (1 - Y_{Cu}\ln(1 - Y_{Cu}))\right] + \Omega Y_{Cu}(1 - Y_{Cu})(1 + KY_{Cu}) \quad (17)$$

Here Ω and K are phenomenological interaction parameters of the used quasiregular model being dependent on P_{O_2} as follows

$$\Omega = A + B\ln(P_{O_2}) \quad \text{and} \quad K = C + D\ln(P_{O_2}) \quad (18)$$

The hyperfree energy of $MO_\gamma^{(l)}$ melt consists of two terms: the hyperfree energy of the solid oxide MO_γ and Gibbs energy of its melting as a function of temperature.

The coefficients in temperature dependencies of Gibbs energy of formation of binary phases (Sr_2CuO_3, $SrCuO_2$ and $Sr_{14}Cu_{24}O_{41}$ in Sr–Cu–O system, Bi_2CuO_3 in Bi–Cu–O system, Ba_2CuO_3 and $BaCuO_2$ in the system Ba–Cu–O) and those of melting of individual oxides, as well as all other phenomenological parameters were calculated by regression analysis of the DTA-data recorded at two values of P_{O_2} in the surrounding atmosphere, namely in pure oxygen ($P_{O_2}=1$) and purified air ($P_{O_2}=0.21$). Their real values are not presented here and the interested reader is refered to original paper [39].

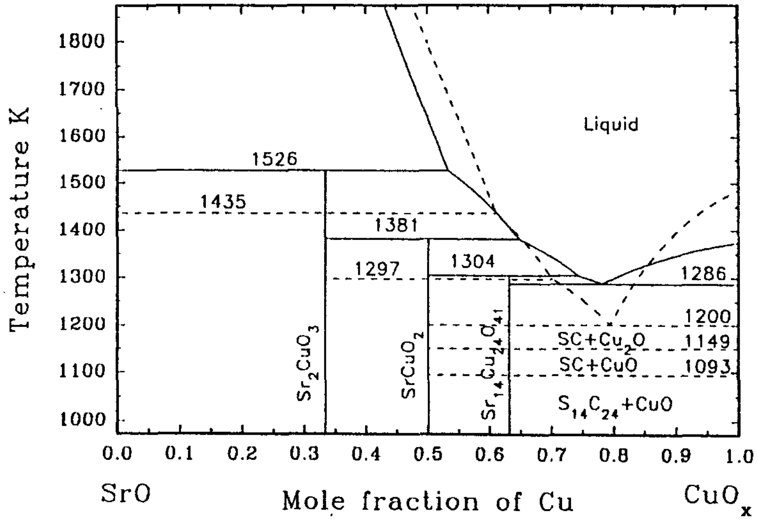

Fig. 1 Phase diagrams of Sr–Cu–(O) system calculated for $P_{O_2}=1$ (full lines) and $P_{O_2}=0.01$ (dashed lines)

The refined parameters were substituted back to model functions of Z_q for the respective phases which were further employed for the numerical calculation of liquidus curves in the phase diagrams. The results are presented on Figs 1, 2 and 3 showing, respectively, the phase diagrams of the systems Sr–Cu–O, Bi–Cu–O and

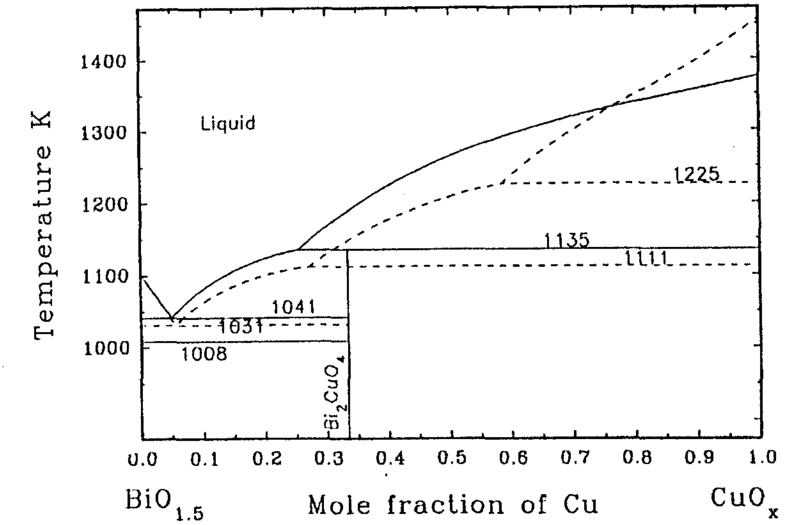

Fig. 2 Phase diagrams of Bi–Cu–(O) system calculated for $P_{O_2}=1$ (full lines) and $P_{O_2}=0.05$ (dashed lines)

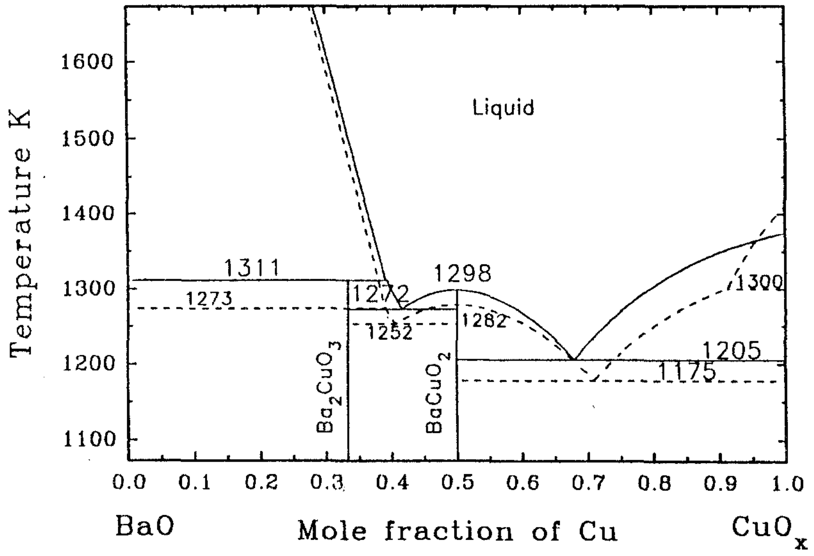

Fig. 3 Phase diagrams of Ba–Cu–(O) system calculated for $P_{O_2}=1$ (full lines) and $P_{O_2}=0.21$ (dashed lines)

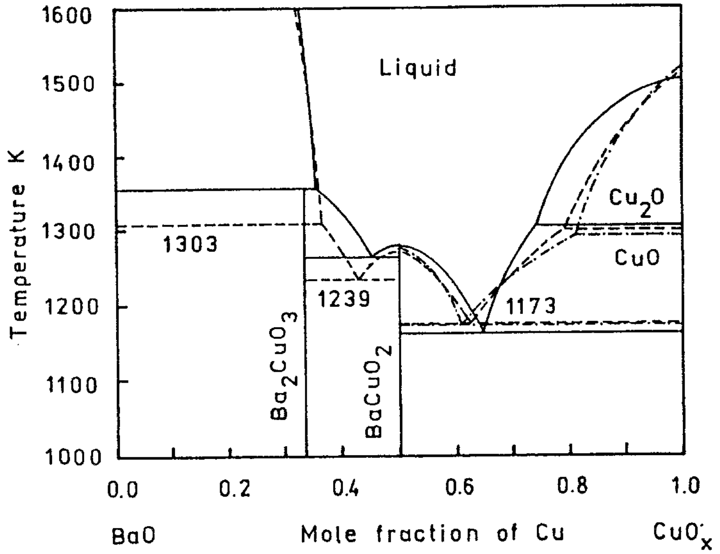

Fig. 4 Phase diagram calculated in Ref. [40] using simple regular model (full line) and in Ref. [41] using temperature dependent subregular model (dashed) together with the experimental data from Ref. [42] (dashed-and-dotted line)

Ba–Cu–O for two values of partial oxygen pressure. In Fig. 4 the previously calculated and experimentally determined diagrams for the system Ba–Cu–O are shown for the comparison.

Let us note that although the calculated curves fit very well the experimental data [39], the thermodynamical properties evaluated from the yielded parameters loose their physical meaning out of the interval of temperatures from which the experimental values were available. Thus a better approach would be based on separate refinement of these parameters for solid phases (e.g. from calorimetric data) whose fixed values would be subsequently used for the regression analysis of the model dependencies of the melt. This improvement is a subject of further investigation.

Thermochemical and thermodynamical data of the $SrO–Bi_2O_3(–CuO_x)$ system and chemical phase diagrams

Currently we have started to calculate thermochemical and thermodynamic properties in the system of $SrO–Bi_2O_3$ [43], see Table 4, trying to extend our estimation to reach preliminary values for the whole $SrO–Bi_2O_3–CuO_x$ system, see Table 5.

Accordingly it was found useful to employ another representation of the effect of oxygen partial pressure against the phase relations involved which is illustrated in the case of $SrO–Bi_2O_3$ in Fig. 5. A recently written computer program [44] enables one to construct generally various types of chemical potential diagrams in the metal (M_1)–metal (M_2)–oxygen systems. For oxides [44] and their relation to HTSC [31]

Table 4 Thermochemical and thermodynamical properties of some double oxides in the SrO–Bi_2O_3 system

Oxides	ΔH^o_{298} / kJ mol^{-1}	S^o_{298} / J mol^{-1} K^{-1}	H^o_{298}–H^o_o / J mol^{-1}	$T_{ph.tr}$/ K	$\Delta H_{ph.tr}$/ kJ mol^{-1}	$c_p=a+b\cdot 10^{-3}T-c\cdot 10^5T^{-2}$/ J mol^{-1} K^{-1}			c_p(at $T>T_{ph.tr}$)/ J mol^{-1} K^{-1}
						a	*b*	*c*	
$Sr_6Bi_2O_9$	–4207.4	471.0	68900	1238	267.7	399.4	68.3	32.0	534.7
$Sr_3Bi_2O_6$	–2443.4	310.2	45065	1483	199.9	254.4	46.8	18.6	356.6
$Sr_2Bi_2O_5$	–1860.3	265.5	37110	1213	132.5	206.0	39.8	14.3	280.6
$Sr_{18}Bi_{22}O_{51}$	–17928.9	2607.0	376330	1076	1099.5	2072.1	411.0	139.7	2777.0
$Sr_6Bi_{14}O_{27}$	–7927.6	1365.7	196020	922	516.7	1054.8	221.5	64.4	1392.0
$SrBi_4O_7$	–1803.5	351.7	50310	800	113.5	266.8	58.7	15.4	346.8
$Sr_2Bi_6O_{11}$	–3029.6	554.5	79450	864	194.9	424.4	90.5	25.0	555.7
$SrBi_2O_4$	–1224.2	202.8	29140	1213	101.5	157.6	32.9	9.9	217.8
$Sr_8Bi_{10}O_{23}$	–8033.1	1175.3	169620	1070	529.8	933.1	185.6	62.7	1250.0
$Sr_8Bi_2O_{11}$	–5387.5	578.1	84770	1335	350.3	496.2	82.9	40.9	670.2
$Sr_5Bi_6O_{14}$	–4902.7	700.0	101975	1213	366.6	565.9	112.6	38.4	775.4
$Sr_6Bi_2O_{11}$	–4391.4	471.0	68900	1238	261.7	399.4	68.3	32.0	534.7
$Sr_6Bi_4O_{15}$	–5162.7	620.4	90130	1200	323.4	508.7	93.6	37.4	685.8
$Sr_{24}Bi_{14}O_{52}$	–19201.2	2332.3	339290	1224	1248.4	1925.4	347.8	143.5	2594.0

Table 5 Thermochemical and thermodynamical properties of some compounds in the Bi–Sr–Cu–O system

Oxides	ΔH^{o}_{298} / kJ mol^{-1}	S^{o}_{298} / J mol^{-1} K^{-1}	$H^{o}_{298}-H^{o}_{o}$ / J mol^{-1}	$T_{ph.tr}$/ K	$\Delta H_{ph.tr}$/ kJ mol^{-1}	$c_p=a+b\cdot10^{-3}T-c\cdot10^{5}T^{-2}$/ J mol^{-1} K^{-1}			c_p(at $T>T_{ph.tr}$)/ J mol^{-1} K^{-1}
						a	*b*	*c*	
$Sr_2Bi_2CuO_6$	–2095.7	303.3	44.5	1372	156.7	247.8	66.0	20.3	384.1
$Sr_8Bi_4Cu_5O_{19}$	–7243.0	956.5	142.2	1819	661.4	849.9	174.2	95.8	1254.9
$Sr_3Bi_2Cu_2O_8$	–2906.4	401.5	59.5	1772	254.1	348.5	78.4	35.9	522.1
$Sr_{18}Bi_{22}Cu_{10}O_{61}$	–2038.4	3072.1	449.6	1676	1438.7	2469	698.3	182.5	3850.4
$Sr_9Bi_4CuO_{16}$	–7097.7	841	120.8	2018	547.2	708	150.6	74.2	1077.8
$Sr_7Bi_2Cu_2O_{12}$	–5384.4	623.1	91.9	2001	477.8	557.2	99	68.9	813.2

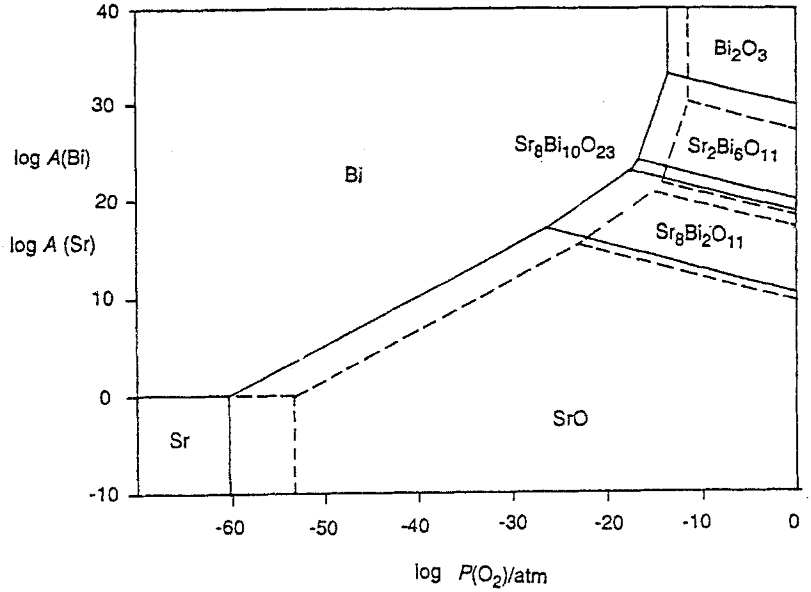

Fig. 5 Chemical potential diagrams in the Bi–Sr–O system calculated [44, 47] for two temperatures 837 K (full) and 937 K (dashed lines)

it was shown that $\log(a_{M_1}/a_{M_2})$ *vs.* $\log P(O_2)$ plot is very convenient and the use of $\log(a_{M_1}/a_{M_2})$ makes it possible to treat the two metallic elements (1 and 2) equivalently. Figure 5 shows such a simplified chemical potential diagram consisting of the stability areas of elements (Bi, Sr), binary (SrO, Bi_2O_3) and selected double ($Sr_2Bi_6O_{11}$, $Sr_8Bi_{10}O_{23}$ and $Sr_8Bi_2O_{11}$) oxides and a similar treatment was already applied in the course of evaluation of the systems Y–Cu–O [31] or Ga–Sb–S [45].

Conclusions

Estimation methods show their importance for computing thermodynamical and thermochemical properties of many inorganic compounds [46] as documanted on the well screened Y–Ba–Cu–O system [20–33]. It certainly would be a useful complementary source of data for existing databases [31, 35, 38, 47].

* * *

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