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Thermodynamic simulation of $YBa_2Cu_3O_x$ deposition from the vapor/gas phase

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Abstract

Thermodynamic simulations were used to study the possibility of $YBa_2Cu_3O_x$ deposition in the system YCl_3–BaI_2–CuCl–H_2O–O_2 and YI_3–BaI_2–CuI–H_2O–O_2 at various temperatures, pressures and initial compositions, taking into account the ratio $\Sigma O/\Sigma Me$ and the different Y–Ba–Cu–O phases.

INTRODUCTION

A survey of the CVD studies concerned with the preparation of high-T_c superconductors (HTSC) [1] has clearly shown that $YBa_2Cu_3O_x$ (123) films are usually prepared from an initial metal–organic compound [2–4] exhibiting a certain level of contamination by carbon.

Using haloid vapors as sources of these metals is more attractive practically. Thermodynamic studies [5] have demonstrated the possibility of such an application, and some 123 films have been obtained experimentally [6]. The purpose of this paper is to recalculate the data published in ref. 5, in addition to a detailed estimation of the conditions for 123 film deposition from haloid vapor sources, based on the computer program complex ASTRA (which makes our thermodynamic simulations possible [7]) and the principles of phase CVD diagram construction [8].

REPRODUCTION OF PREVIOUS RESULTS BY OTTOSSON ET AL. [5]

According to ref. 5, YCl_3, BaI_2 and CuCl were chosen as sources of these metals, oxygen being supplied by O_2 and/or H_2O. The ratio $YCl_3 : BaI_2 : CuCl$ equaled 1 : 2 : 3 and complied with the composition of the

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initial mixture according to the equation $\Sigma O/\Sigma Me = \{[H_2O]$ $[O_2]\}/\{[YCl_3] + [BaI_2] + [CuCl]\}$ which was varied over a wide range. The minimization of the system's free energy was realized by the computer program AKVICALC [5]. Calculations were performed at different pressures and temperatures. For the system studied, the thermodynamic functions of the condensed and gaseous substances were taken from the literature (Table 1). As indicated in ref. 5 the properties of 123 were based on ref. 9, but the oxygen index X was not specified.

The CVD diagrams produced by calculation show the temperature–concentration regions in which 123 deposits simultaneously with at least one other condensed phase. According to our new data, varying the values of the concentration of the initial substances listed in Table 1, in addition to the pressure and temperature, allow the evaluation of regions of the CVD diagrams in which deposition is almost entirely limited to 123 only. According to ref. 5, typical CVD diagrams are as shown in Fig. 1. A detailed analysis allows the following comments.

The calculation in ref. 5 did not take into account the properties of all condensed phases which can be identified in the system Y–Ba–Cu–O, particularly $BaCuO_2$, Y_2BaCuO_5, $Y_2Cu_2O_5$, $YCuO_2$, etc.

It is not clear which composition of 123 the authors in ref. 5 were referring to, because ref. 9 gives the standard enthalpies of formation of

TABLE 1

Substances included in thermodynamic calculations in ref. 5

Condensed			
1 $YBa_2Cu_3O_{7-y}$	6 CuCl	11 Y_2O_3	16 YI_3
2 YOCl	7 CuO	12 BaO_2	17 Ba
3 $BaCl_2$	8 $Cu(OH)_2$	13 Cu	18 BaI_2
4 BaH_2	9 Y	14 $CuCl_2$	19 BaO_2
5 $Ba(OH)_2$	10 YCl_3	15 Cu_2O	20 CuI
Added: $Y_2Ba_2O_5$			
Gaseous			
1 YCl_2	12 H_2O_2	23 I_2	34 Cu_2
2 Y_2O_2	13 O_3	24 Cl_2O	35 Cu_2Cl_2
3 $BaCl_2$	14 Y	25 HCl	36 Cu_5Cl_5
4 CuCl	15 YCl_3	26 HO_2	37 CuI
5 Cu_3Cl_3	16 YO	27 O	38 Cu_4I_4
6 CuO	17 BaI_2	28 OH	39 Cl_2
7 Cu_2I_2	18 BaO1	29 YCl	40 ICl
8 I	19 Cu	30 YI_3	41 H
9 ClO	20 Cu_4Cl_4	31 Y_2O	42 HClO
10 H_2	21 Cu_3I_3	32 Ba	43 H_2O
11 HI	22 Cl	33 BaI_2	44 O_2

Added: ClO_2, IO, ICl, BaH, Ba(OH), $Ba(OH)_2$, BaCl, YO_2, Ba, ClOH, BaIOH, CuH, $CuCl_2$ and Ba_2

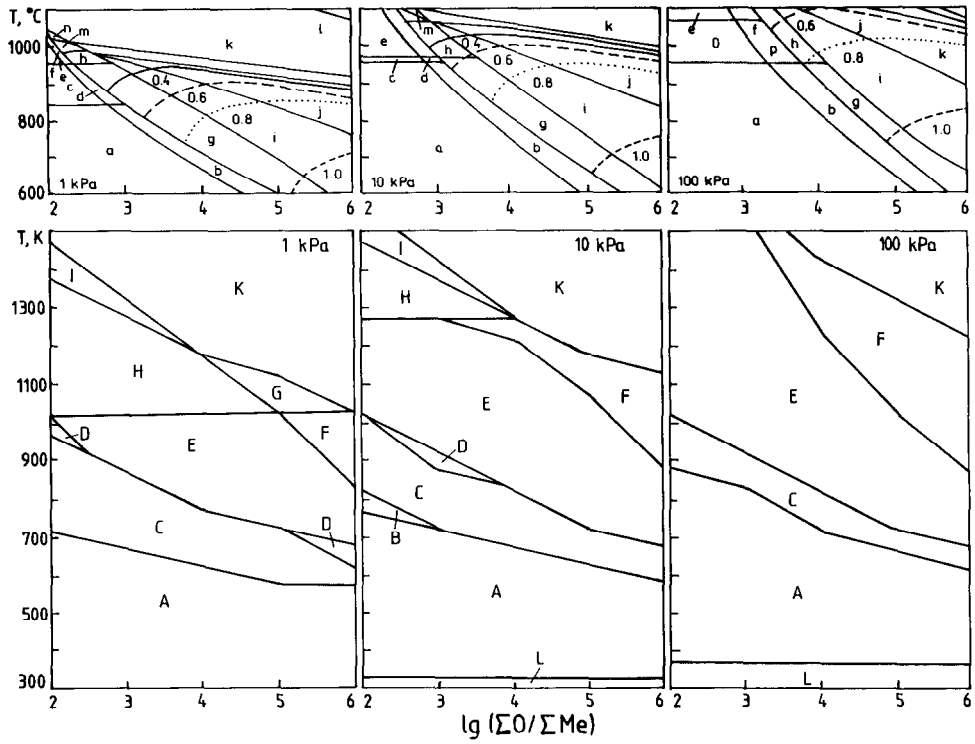

Fig. 1. Comparison of CVD diagrams for the system YCl_3–BaI_2–CuCl–H_2O–O_2 calculated by Ottosson et al. [5] (upper part), with our data (lower part) at the total pressures shown. The yield of 123 in the upper part is indicated by dotted lines. Compositions of individual regions are listed in Table 2.

the phases with x equal to 6.25, 6.47, 6.69 and 6.93. Lack of further information about the other thermodynamic data in ref. 9 casts doubt on the derivation of other thermodynamic and thermochemical properties of 123 in ref. 5 (such as S°_{298} and $C_p(T)$.

We have deduced that the phase of 123 with X equal to 6.93 was employed.

Sources of information about the properties of the gaseous phases CuI, Cu_2I_2, Cu_3I_3 and Cu_4I_4 given in ref. 5 were insufficient for a complete thermodynamic description of these substances.

The program EKVICALC was not described in enough detail, so it is indistinguishable from already known programs which allow estimation of the composition and properties of equilibria for multicomponent heterogeneous systems [7].

CALCULATION OF CVD DIAGRAMS IN THE YCl_3–BaI_2–CuCl–H_2O–O_2 SYSTEM

In an attempt to reproduce the results of Ottosson et al. [5], we used the same set of condensed and gaseous phases as they did (Table 1). To the

TABLE 2

Phases in the CVD diagrams shown in Fig. 1

Region	Phases present				Region	Phases present				
a	Y_2O_3	CuO	$BaCl_2$(s)		A	Y_2O_3				
b	Y_2O_3	CuO	$BaCl_2$(s)	$YBa_2Cu_3O_x$	B	Y_2O_3	$YBa_2Cu_3O_7$			
c	Y_2O_3	Cu_2O	$BaCl_2$(s)		C		$YBa_2Cu_3O_7$			
d	Y_2O_3	Cu_2O	$BaCl_2$(s)	$YBa_2Cu_3O_x$	D		$YBa_2Cu_3O_7$	CuO		
e	Y_2O_3	Cu_2O	$BaCl_2$(s)		E		$YBa_2Cu_3O_7$	CuO	$Ba(OH)_2$	
f	Y_2O_3	Cu_2O	$BaCl_2$(s)	$YBa_2Cu_3O_x$	F	Y_2O_3	$YBa_2Cu_3O_7$		$Ba(OH)_2$	
g	Y_2O_3	Cu_2O	$BaCl_2$(l)	$YBa_2Cu_3O_x$	G	Y_2O_3	$YBa_2Cu_3O_7$	CuO		
h	Y_2O_3		$BaCl_2$(s)	$YBa_2Cu_3O_x$	H	Y_2O_3		CuO	$Ba(OH)_2$	
i	Y_2O_3		$BaCl_2$(l)	$YBa_2Cu_3O_x$	I		$YBa_2Cu_3O_7$	CuO		$Y_2Cu_2O_5$
j	Y_2O_3			$YBa_2Cu_3O_x$	K			CuO		$Y_2Cu_2O_5$
k	Y_2O_3			$YBa_2Cu_3O_x$	L	Y_2O_3				$Y_2Cu_2O_5$
l	Y_2O_3				M	Y_2O_3	$YBa_2Cu_3O_7$	Cu_2O		
m	Y_2O_3		$BaCl_2$(l)	$YBa_2Cu_3O_x$	N	Y_2O_3	$YBa_2Cu_3O_7$			$Y_2Cu_2O_5$
n	Y_2O_3		$BaCl_2$(l)		O			Cu_2O		$Y_2Cu_2O_5$
o	Y_2O_3	CuO	$BaCl_2$(l)		P		$YBa_2Cu_3O_7$		$Ba(OH)_2$	
p	Y_2O_3	CuO	$BaCl_2$(l)	$YBa_2Cu_3O_x$	Q		$YBa_2Cu_3O_7$	CuO	BaO_2	

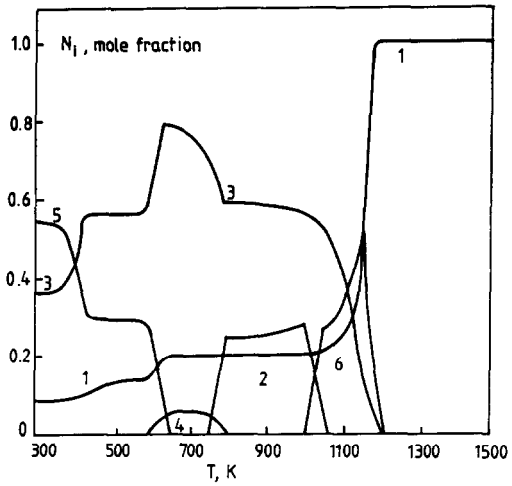

Fig. 2. Calculated content of deposited phase plotted against temperature at $P = 10^5$ Pa and lg ($\Sigma O/\Sigma Me$) = 4. The regions correspond to 1, Y_2O_3; 2, $Ba(OH)_2$; 3, $BaCl_2$; 4, $YBa_2Cu_3O_x$; 5, CuO; 6, BaO_2.

gaseous components, for completion, we added ClO_2, IO, ICl, BaH, Ba(OH), $Ba(OH)_2$, BaCl, YO_2, BAClOH, BaIOH, CuH, $CuCl_2$ and Ba_2; $Y_2Cu_2O_5$ was added to the condensed phases. Thermodynamic functions of condensed CuI, YCl_3, YI_3, YOCl and BaO_2, in addition to those of gaseous CuI, Cu_2I_2, Cu_3I_3 and Cu_4I_4 have been calculated elsewhere [10] similarly to those of 123 ($x = 7$) [11]. For the remainder of the substances, the thermodynamic properties were taken from the databases ASTRA and IVTANTERMO. The simulation was performed at the initial composition and conditions of ref. 5, a temperature range of 300–1500 K with steps of 50 K, pressures (P) of 10^5, 10^6 and 10^7 Pa (i.e. about 1.1–100 atm), and at various values of lg($\Sigma O/\Sigma Me$). Results of the calculation for a single composition are shown in Fig. 1. CVD diagrams are shown in Fig. 2.

It is estimated that 123 exists within the temp. range 550–1050 K. With the increase of lg($\Sigma O/\Sigma Me$), the region of phase existence narrows and shifts towards lower temperatures. Content of 123 in the mixture of concomitant phases ($BaCl_2$, Y_2O_3 and $Ba(OH)_2$) is rather low. Attempts to increase the 123 content in the mixture of co-depositing phases following the recommendation given in ref. 5 failed: we were unable to reproduce these results by producing any significant increase in the yield of the 123 phase, though the qualitative agreement of deposition fields was reproduced in a number of cases. This disagreement can be related to the following facts.

The number of components in our calculations is greater by the 14 added substances.

The sources of data about the thermodynamic functions of some components in question were different; for some of the components, the calcu-

lated properties [10] were found to be different (such as $H^{\circ}_{298}(CuI_{(g)})$ from ref. 12 in addition to data from other research dealt with in detail in ref. 10).

As mentioned above, the 123 phase in ref. 5 is described vaguely and its thermodynamic functions are not fully specified.

THERMODYNAMIC SIMULATION OF THE YI_3–BaI_2–CuI–H_2O–O_2 SYSTEM WITHOUT TAKING ACCOUNT OF THE Y–Ba–Cu PHASES

In this section we restrict our consideration to the CVD study using metal iodides only. The research was performed in two stages. First, we identified in the Y–Ba–Cu–O system only the 123 and $Y_2Cu_2O_5$ phases. Furthermore, the components of the systems were not the same as the substances considered above, because the chlorine-containing components were omitted. Conditions for the ratio ($\Sigma O/\Sigma Me$), temperature T and pressure P remained analogous to those in Fig. 1. The CVD-diagrams obtained are shown in Fig. 3, where the compositions of the individual regions correspond to those listed in Table 2. It is estimated that 123 deposits in the range 350–1500 K, in some regions the phase yield being

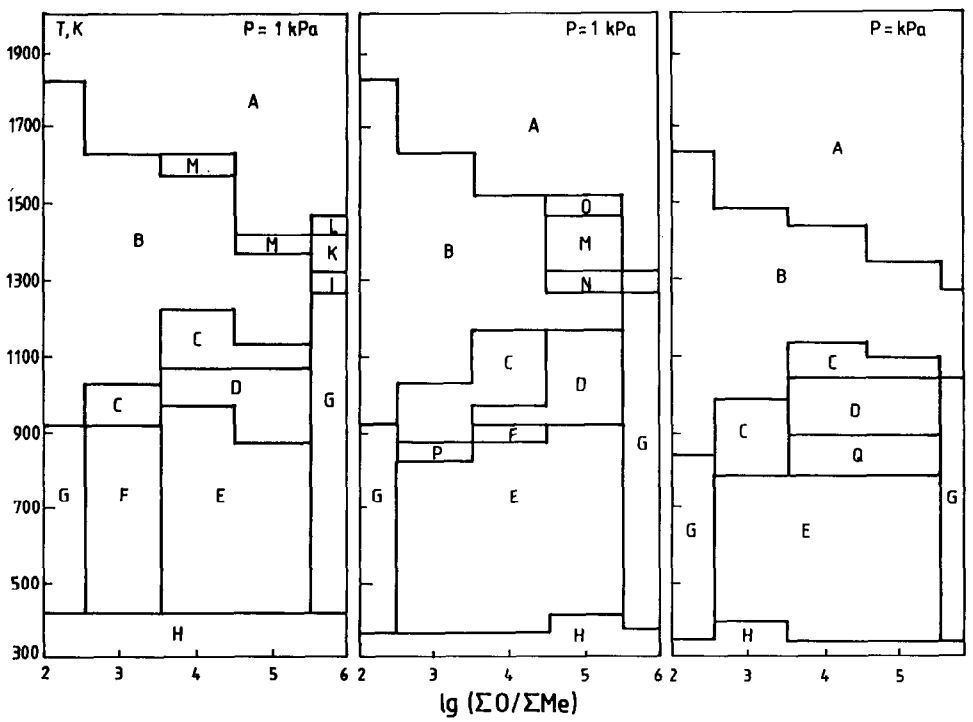

Fig. 3. CVD diagrams for YI_3–BaI_2–CuI–H_2O–O_2 at the total pressures shown, taking no regard for the phases in the Y–Ba–Cu–O system (except $YBa_2Cu_3O_x$ and $Y_2Cu_2O_5$).

TABLE 3

Estimated phases [a] with ΔH_{melt} [b] and T_{melt} [b] (theoretically calculated values plus known experimental data)

Formula [c]	Theor. calc.		Exp.	Formula [c]	Theor. calc.		Exp.
	ΔH_{melt}	T_{melt}	T_{melt}		ΔH_{melt}	T_{melt}	(stoich.) [c]
$BaCuO_2$ [d]	45.0	1007	1010 [e]	$Y_2Ba_6Cu_4O_{13}$ [f]	328.63	1222	(132)
Ba_2CuO_3 [g,h]	71.76	1087		$YBa_2Cu_4O_8$ [h]	226.17	1442	(124) [e,i]
Ba_3CuO_4	92.79	1042	820 [k,l]	$Y_2Ba_4Cu_8O_{15}$ [h]	836.86	1367	(850°C) [e,i]
$Ba_2Cu_3O_5$ [g,h]	89.15	741		$Y_2Ba_4Cu_7O_{14}$ [h,d]	390.50	1366	(247)
$Ba_3Cu_5O_8$ [g,h]	142.22	738		$Y_2Ba_4Cu_7O_{15}$ [h,d]	404.97	1366	(950°C) [e,i]
				$Y_6Ba_{16}Cu_{10}O_{35}$ [f,l]	880.69	1227	(385)
$Y_2Ba_4O_7$ [l,m]	160.02	1127	1150 [e]	$Y_2Ba_2Cu_4O_9$	251.12	1412	(112) [j]
Y_2BaO_4	99.1	1337	1400 [e]	$Y_2Ba_4Cu_6O_{13}$ [d]	328.83	1267	(123) [n]
$Y_2Ba_2O_5$ [m]	120.66	1250	1000 [e]	$Y_2Ba_8Cu_4O_{15}$ [g]	369.74	1177	(142)
$Y_4Ba_3O_9$	218.76	1280	2160	$Y_2Ba_{10}Cu_4O_{17}$ [g]	297.64	810	(152)
				$Y_2Ba_{10}Cu_6O_{19}$ [g]	471.73	1177	(153)
Y_2CuO_4	113.25	1567		$Y_2Ba_6Cu_2O_{11}$ [g]	265.86	1167	(131)
$Y_2Cu_2O_5$	118.7	1227	1140 [e]	$Y_2Ba_4Cu_2O_9$ [g]	225.71	1237	(121)
$YCuO_2$ [d,h]	54.85	1287		$Y_2Ba_8Cu_6O_{17}$ [f,l]	370.23	1003	(143)
				$Y_4BaCu_5O_{12}$ [a]	259.58	1069	
$YBa_2Cu_3O_7$ [d]	171.78	1230	1010 [e,i,j,m]	$Y_2Ba_6Cu_6O_{15}$	322.8	993	(133)
$YBa_2Cu_3O_6$ [d]	152.57	1170		$Y_2Ba_3Cu_5O_{11}$ [g]	233.94	994	(235)
Y_2BaCuO_5	122.25	1272	1260 [i]	$Y_2Ba_{12}Cu_6O_{21}$ [a]	547.57	1246	
				$Y_2BaCu_3O_7$ [g]	149.62	1036	(213)

[a] Including hypothetical phases. [b] ΔH_{melt} in kJ and T_{melt} in °C. [c] Simplified cation ratio. [d] Oxygen nonstoichiometry (O_y). [e] Incongruent melting. [f] Reported as traced experimentally. [g] Existence assumed in literature. [h] Existing at a P_{O_2} different from 1 atm. [i] Prepared as a single phase. [j] Found as Pt-substituted (rather than Cu-based). [k] Decomposition temperature. [l] Oxycarbonated. [m] Metastable. [n] $YBa_2Cu_3O_{6.5}$.

close to 100%. With the pressure increase, the 123 region shifts towards lower temperatures and narrows.

It is evident that the mere use of iodides as metal sources provides much better prospects of 123 deposition than the complex utilization of Y and Cu chlorides with Ba iodide. In order to check this, and to make the CVD-diagrams more accurate, we extended our calculations to cover the existence of the various Y–Ba–Cu–O compounds [14–18] (see Table 3).

TABLE 4

Phases in the CVD diagram in Fig. 5

Region	Phases
A	CuO, $Y_4BaCu_5O_{12}$, $Ba(OH)_2$
B	CuO, $Y_4BaCu_5O_{12}$, $Y_2Ba_6Cu_2O_{11}$
C	CuO, $Y_4BaCu_5O_{12}$, $BaCuO_2$
D	$Y_4BaCu_5O_{12}$, $BaCuO_2$, $Y_2Ba_6Cu_2O_{11}$
E	$Y_5BaCu_5O_{12}$, $BaCuO_2$, $Y_2Ba_4Cu_8O_{15}$
F	$BaCuO_2$, $Y_2Ba_4Cu_8O_{15}$, $YBa_2Cu_3O_6$
G	$Y_4BaCu_5O_{12}$, $Y_2Ba_6Cu_2O_{11}$, $YBa_2Cu_3O_6$
H	$Y_2Ba_6Cu_2O_{11}$, $YBa_2Cu_3O_6$
I	$Y_4BaCu_5O_{12}$, $YBa_2Cu_3O_6$
J	$Y_4BaCu_5O_{12}$, Y_2CuO_4, $YBa_2Cu_3O_6$
K	$BaCuO_2$, $YBa_2Cu_3O_6$
L	CuO, $BaCuO_2$, $YBa_2Cu_3O_6$
M	CuO, $YBa_2Cu_3O_6$
N	$YBa_2Cu_3O_6$
O	Y_2CuO_4, $YBa_2Cu_3O_6$
P	CuO, Y_2CuO_4, $YBa_2Cu_3O_6$
Q	Y_2CuO_4, $Y_2Ba_8Cu_6O_{17}$
R	Y_2CuO_4
S	$YCuO_2$, Y_2CuO_4, $Y_2Ba_8Cu_6O_{17}$
T	$YCuO_2$, $Y_2Ba_8Cu_6O_{17}$
U	$YCuO_2$, Y_2CuO_4
V	$YCuO_2$, Y_2CuO_4, Y_2BaO_4
W	$BaCuO_2$, Y_2BaCuO_5, $YBa_2Cu_3O_6$
X	$Y_4BaCu_5O_{12}$, $BaCuO_2$, Y_2BaCuO_5
Y	Y_2CuO_4, Y_2BaO_4
Z	Y_2BaO_4
α	$Y_2Ba_8Cu_6O_{17}$, Y_2BaO_4
β	Y_2BaCuO_5, Y_2CuO_4, $YBa_2Cu_3O_6$
γ	Y_4BaCuO_5, Y_2CuO_4, $YBa_2Cu_3O_6$
δ	$Y_4BaCu_5O_{12}$, $Y_2Ba_4Cu_8O_{15}$, $YBa_2Cu_3O_6$
ϵ	CuO, $Y_4BaCu_5O_{12}$
μ	Y_2BaCuO_5, Y_2BaO_4, $YBa_2Cu_3O_6$
π	$Y_2Ba_6Cu_2O_{11}$, Y_2CuO_4, $YBa_2Cu_3O_6$

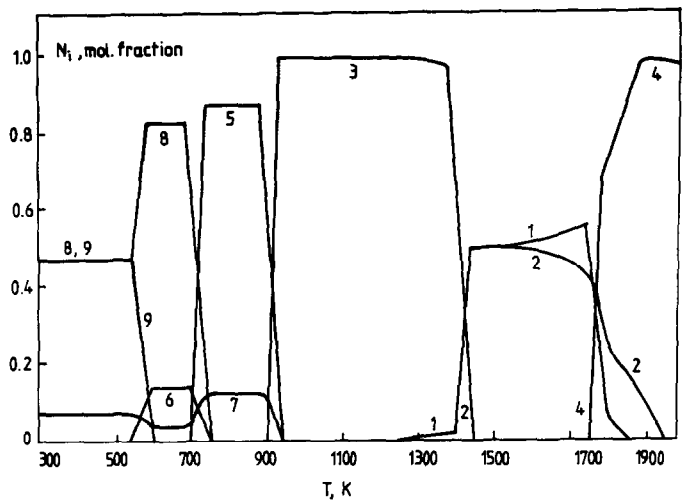

Fig. 4. Content of co-depositing phases related to temperature at $P = 10^5$ Pa and $\lg(\Sigma O/\Sigma Me) = 3$ for the system YI_3–BaI_2–CuI–H_2O–O_2, taking into account the possible phases in the Y–Ba–Cu–O system. The regions correspond to 1, $Y_2Cu_2O_5$; 2, $Y_2Ba_8Cu_6O_{18}$; 3, $YBa_2Cu_3O_x$; 4, $YCuO_2$; 5, $BaCuO_2$; 6, $Y_2Ba_6Cu_2O_{11}$; 7, $Y_4BaCu_5O_{12}$; 8, CuO; 9, $Ba(OH)_2$.

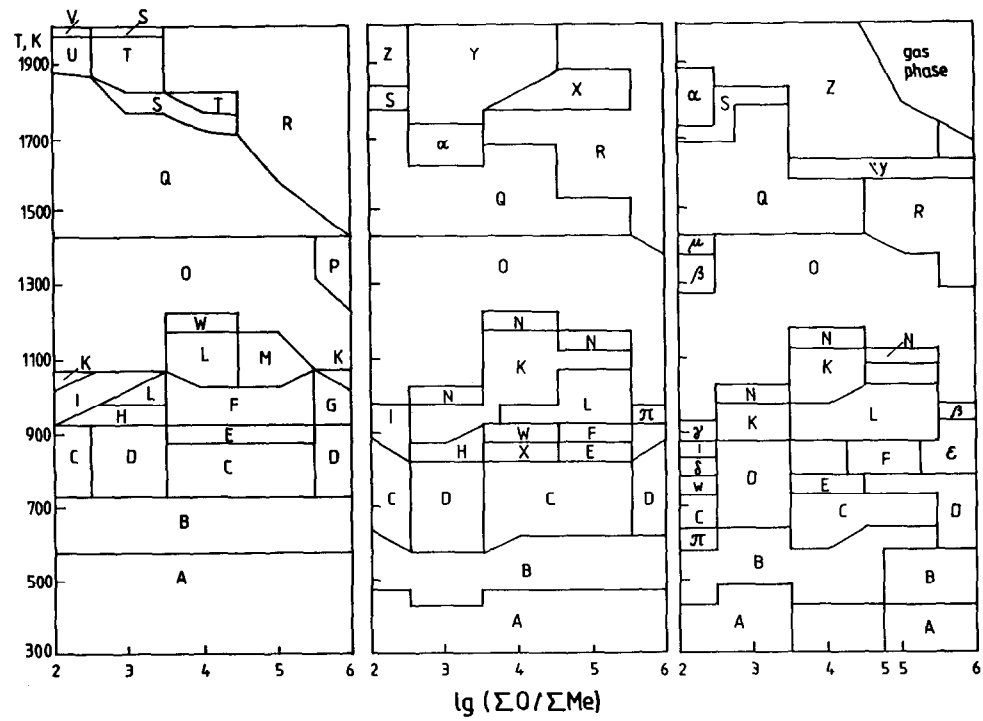

Fig. 5. CVD diagram for the system YI_3–BaI_2–CuI–H_2O–O_2 at total pressures of 10^5, 10^4 and 10^3 Pa, taking into account all the Y–Ba–Cu–O phases listed in Table 4.

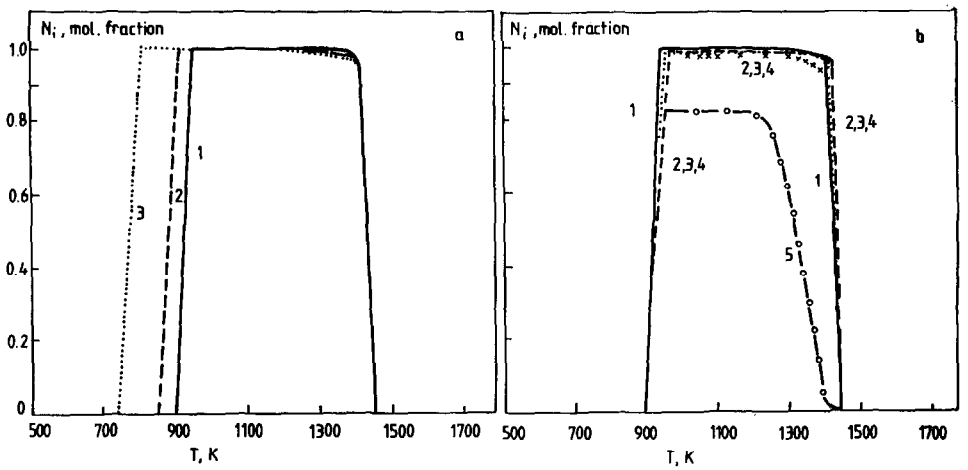

Fig. 6. System YI_3–BaI_2–CuI–H_2O–O_2, taking into account all the Y–Ba–Cu–O phases listed in Table 4. (a) Yield of 123 ($6 < x < 7$) related to temperature and pressure (where 1–3 signify 10^5, 10^4 and 10^3 Pa, respectively.) (b) Yield of 123 ($6 < x < 7$) related to temperature and lg($\Sigma O/\Sigma Me$) (where regions 1–5 represent the rations 3, 2, 4, 5 and 6 respectively).

SIMULATION TAKING INTO ACCOUNT THE PHASES POSSIBLY IDENTIFIABLE IN THE Y–Ba–Cu–O SYSTEM

The condensed phases were added in accordance with Table 3, assuming all the experimentally traced [16–18] and hypothetically predicted phases [14,15]. The thermodynamic functions were calculated by the method described in refs. 11 and 13. Conditions of CVD simulation were similar to those used above. Some of the results obtained are shown in Figs. 4 and 5. It is worth noting that 123 ($x = 7$) deposition was not observed, but that there are regions where deposition of 123 ($x = 6$) is possible in rather high yield. It is evident that the introduction of additional phases considerably changes the content and composition of the deposited phases with regard to the regions marked in Figs. 4 and 5.

Changes of pressure and composition of the initial gas mixture (see Fig. 6) can lead to changes of the temperature boundaries of the 123 deposition region and can produce a nonstoichiometric 123 ($6 < x < 7$). The data obtained can form the basis of a practical method of preparation of 123 films in the recommended YI_3–BaI_2–CuI–H_2O–O_2 system, assuming subsequent formation of the superconductor by the standard film–P_{O_2}–T method [1].

CONCLUSIONS

Thermodynamic simulation was used to study the possibility of 123 deposition in the systems YCl_3–BaI_2–CuCl–H_2O–O_2 and YI_3–BaI_2–

$CuI-H_2O-O_2$ at various temperatures, pressures and initial compositions according to the ratio ($\Sigma O/\Sigma Me$), and having regard for the number of Y–Ba–Cu–O phases. For the system $YI_3-BaI_2-CuCl-H_2O-O_2$ and with $Y_2Ba_2O_5$ as the only phase, the $BaCl_2$, CuO and $Ba(OH)_2$ were found to deposit with 10 mol% of 123 ($x = 7$), which did not confirm the results of Ottosson et al. [5]. In contrast, the $YI_3-BaI_2-CuCl-H_2O-O_2$ system shows regions of 123 ($x = 7$) deposition close to 100 mol% yield. When the additional Y–Ba–Cu–O compounds were introduced besides the originally assumed $Y_2Ba_2O_5$, the deposition regions of 123 ($x = 7$) were not identified. However, other regions of 123 ($6 < x < 7$) deposition were found to provide high yields (close to 100 mol%) and the conditions for 123 ($x = 6$) deposition were estimated.

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