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PHASE DIAGRAM OF THE PSEUDOBINARY $BaCuO_2$–$YBa_2Cu_3O_{6.5}$–$YCuO_{2.5}$ SYSTEM

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ABSTRACT

The recent discovery of high temperature superconductors has led to the study of the phase equilibria in the corresponding systems, particularly Y–Ba–Cu–O. Obviously the investigation of pseudobinary regions is a necessity for a complete understanding of such a complex system. In this work the $YCuO_{2.5}$–$BaCuO_2$ tie line, including the superconductive 1 : 2 : 3 phase, in the temperature range 900–1300 °C at $PO_2 = 100$ kPa was investigated using X-ray phase analysis and DTA. Samples were heated in an oxygen atmosphere at various temperatures and were subsequently quenched. The resulting pseudobinary phase diagram of the $YCuO_{2.5}$–$BaCuO_2$ system was constructed assuming that copper ions were present as Cu^{2+}; deviations from stoichiometry were neglected.

INTRODUCTION

The $YO_{1.5}$–BaO–CuO system has not been described fully and is not completely understood even though intense activity has been devoted to the study of superconductive phases. The known compounds in the $YO_{1.5}$–BaO–CuO system include the end member oxides and the binary compounds barium cuprate $BaCuO_2$ (0 : 1 : 1) reported by Midgeon [1] and yttrium cuprate $YCuO_{2.5}$ (1 : 0 : 1) reported by Lambert [2]. Most important are the ternary compounds Y_2BaCuO_5 (2 : 1 : 1) (initially reported by Michel and Raveau [3] as the insulating "green phase") and $YBa_2Cu_3O_{7-y}$ (1 : 2 : 3) (isolated as a single superconductive phase [4–6]). The binary phase diagram $YO_{1.5}$–BaO has been studied by Kwestroo et al. [7]. This has been modified by Anderson, as reported in ref. 8, where four possible barium yttrium oxides are presented: $Y_2Ba_4O_7$ (1 : 2 : 0), $Y_2Ba_2O_5$ (1 : 1 : 0), $Y_4Ba_3O_9$ (4 : 3 : 0) and Y_2BaO_4 (2 : 1 : 0); these are mutually stable within different temperature regions. The CuO–BaO and CuO–$YO_{1.5}$ binaries have also been reported [8] and show the above-mentioned cuprate phases and the CuO to Cu_2O transition at 1026 °C in air. The ternary diagram has been described by Frase et al. [9,10] and includes the additional binary com-

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pounds 0 : 1 : 1, Ba_2CuO_3 (0 : 2 : 1) and Ba_3CuO_4 (0 : 3 : 1) and the ternary compound $YBa_3Cu_2O_{6.5}$ (1 : 3 : 2). Some other studies have been carried out to describe the phase relations in this ternary system [6,11,12] and show, for example, that the 1 : 2 : 3 phase is in equilibrium with the 2 : 1 : 1 phase and CuO at 950–1000 ° C [12] and that the 2 : 1 : 1 phase is in equilibrium with the 0 : 1 : 1 phase at 950 ° C [11]; this relation breaks down at 1000 ° C [8,10]. Metastable phases are supposed to occur as 1 : 1 : 2 [13] (analogous to $La_3Ba_3Cu_6O_{13.5}$ [14]) or 4 : 1 : 5 (analogous to $La_4BaCuO_5O_{12}$ [15]). Roth et al. [8] have reported a compound with a composition close to 1 : 3 : 2 which transforms from a low ordered to a high ordered perovskite structure; both modifications coexist in quenched samples within the range 950–1075 ° C. The 1 : 2 : 3 phase melts incongruently at 1010 ° C. The 2 : 5 : 5 composition displays a liquid phase at 960 ° C below which the 1 : 2 : 3, 2 : 1 : 1 and 0 : 1 : 1 phases coexist. The decomposition of the 1 : 3 : 2 compound at the temperatures 900, 950 and 1000 ° C leads to the formation of the 0 : 1 : 1, 2 : 1 : 1 with 0 : 1 : 1 and 2 : 1 : 1 phases, respectively. The 1 : 2 : 1 phase decomposes at 900 ° C to the 2 : 1 : 1 and Y_2BaO_4 phases with the uncertain presence of 1 : 3 : 2 and at 950 ° C to the 2 : 1 : 1 and $Y_4Ba_3O_9$ phases with the uncertain presence of 1 : 3 : 2. Takayama-Muromachi et al. [16] have reported the existence of the 2 : 1 : 3 phase. Another superconductive phase 1 : 4 : 2 has also been reported [17].

From the review above it follows that the phase relations in the ternary $YO_{1.5}$–BaO–CuO system are not completely clear. A thorough study of the individual pseudobinary regions in this system will allow the determination of the phase relations. In this study we have investigated the $YCuO_{2.5}$–$BaCuO_2$ tie line because it includes the superconductive 1 : 2 : 3 compound.

EXPERIMENTAL

Preparation of samples

Powdered Y_2O_3, $Ba(OH)_2 \cdot xH_2O$ and CuO reagents (pure per analysis) (Lachema Brno) were used as starting materials. These reagents were chemically analysed using spectroscopic and volumetric methods and corrections for volatile impurities were taken into account. A large number of samples of various compositions were prepared by mixing the starting materials in given ratios. The samples were then ground, preheated for 24 h at 900 ° C, ground again and pressed into pellets of about 10 mm in diameter and 5 mm thickness. The pellets were placed into a Pt micro-boat, sintered at the required temperature in a Kanthal horizontal furnace in an oxygen atmosphere and quenched to room temperature by removing and placing the micro-boat onto a metallic block. The sequence of operations was repeated until the equilibrium state was reached, i.e. no structural or phase composition changes were observed. The total sintering time did not exceed 125 h at the temperatures below 1000 °C and 50 h at higher temperatures.

TABLE 1

Observed and calculated interplanar spacings for the $YCuO_{2.5}$ phase (orthorhombic structure, space group *Pna* 2_1 [18], lattice parameters $a = 10.790$ Å, $b = 3.497$ Å, $c = 12.452 \pm 0.0004$ Å)

h	k	l	d_o (Å)	d_c (Å)	I/I_0
2	0	2	4.097	4.096	7
2	0	3	3.299	3.302	13
1	1	1	3.224	3.225	2
0	0	4	3.122	3.124	3
2	1	0	2.941	2.944	28
1	1	2	2.941	2.943	
2	1	1	2.864	2.865	80
4	0	0	2.701	2.706	100
4	0	1	2.646	2.644	8
1	1	3	2.600	2.603	3
3	1	1	2.466	2.464	2
2	1	3	2.403	2.402	4
3	1	2	2.336	2.331	2
4	0	3	2.268	2.267	11
2	0	5	2.268	2.267	
4	1	0	2.144	2.141	2
2	1	4	2.144	2.140	
4	1	1	2.110	2.110	2
0	0	6	2.079	2.080	4
4	1	2	2.025	2.024	32
2	0	6	1.9411	1.9408	11
4	1	3	1.9013	1.9028	24
2	1	5	1.9013	1.9023	
4	0	5	1.8337	1.8331	4
5	1	2	1.7626	1.7644	20
4	1	4	1.7626	1.7642	
1	1	6	1.7626	1.7638	
0	2	0	1.7529	1.7513	14
6	0	2	1.7307	1.7306	3
1	2	1	1.7115	1.7123	1
2	1	6	1.6946	1.6971	3
2	0	7	1.6946	1.6921	
6	0	3	1.6529	1.6527	13
6	1	0	1.6032	1.6016	16
3	1	6	1.6032	1.6010	
6	1	1	1.5866	1.5885	11
0	1	7	1.5866	1.5878	

TABLE 2

Observed and calculated interplanar spacings for the Y_2BaCuO_5 phase (orthorhombic structure, space group *Pnma* [19], lattice parameters $a = 12.182$ Å, $b = 15.658$ Å, $c = 7.141 \pm 0.0007$ Å)

h	k	l	d_o (Å)	d_c (Å)	I/I_0
2	1	1	3.583	3.584	4
1	0	2	3.424	3.425	8
2	0	2	3.079	3.079	15
4	0	0	3.048	3.045	
3	1	1	2.998	2.994	100
1	1	2	2.935	2.930	68
0	2	0	2.836	2.828	44
4	0	1	2.806	2.801	24
2	1	2	2.706	2.705	18
1	2	1	2.574	2.570	4
2	2	0	2.574	2.565	
4	1	1	2.512	2.510	14
3	1	2	2.423	2.423	9
2	2	1	2.423	2.414	
1	0	3	2.338	2.336	5
5	0	1	2.307	2.305	14
0	2	2	2.217	2.217	23
2	0	3	2.217	2.217	
0	1	3	2.196	2.194	4
1	2	2	2.183	2.181	9
1	1	3	2.161	2.159	6
4	1	2	2.137	2.144	3
5	1	1	2.137	2.135	
2	2	2	2.074	2.083	13
4	2	0	2.074	2.072	
2	1	3	2.074	2.064	
6	0	0	2.032	2.030	9
4	2	1	1.9935	1.9901	33
6	0	1	1.9489	1.9526	9
3	2	2	1.9489	1.9457	
4	0	3	1.8769	1.8752	13
6	1	1	1.8466	1.8458	4
5	2	1	1.7857	1.7871	12
0	0	4	1.7857	1.7850	
4	1	3	1.7792	1.7799	4
1	0	4	1.7696	1.7661	4
6	0	2	1.7696	1.7647	
2	3	1	1.7445	1.7465	17
2	2	3	1.7445	1.7447	
5	0	3	1.7009	1.7024	2
7	0	1	1.6908	1.6906	5
6	1	2	1.6865	1.6846	9
1	1	4	1.6865	1.6859	
3	3	1	1.6639	1.6631	18
1	3	2	1.6529	1.6519	15
6	2	0	1.6529	1.6492	

TABLE 2 (continued)

h	k	l	d_o (Å)	d_c (Å)	I/I_0
5	2	2	1.6340	1.6396	2
1	1	4	1.6340	1.6395	
3	0	4	1.6340	1.6341	
5	1	3	1.6340	1.6302	
7	1	1	1.6208	1.6198	9
2	3	2	1.6091	1.6082	6
6	2	1	1.6091	1.6069	
4	3	0	1.5989	1.6032	4
4	3	1	1.5631	1.5642	16
7	0	2	1.5631	1.5642	
4	2	3	1.5631	1.5629	
6	0	3	1.5429	1.5446	4
3	3	2	1.5429	1.5424	
4	0	4	1.5429	1.5400	

TABLE 3

Observed and calculated interplanar spacings for the YBa$_2$Cu$_3$O$_{6.5}$ phase quenched from 950 °C (tetragonal structure, space group $P4/mmm$, lattice parameters $a = 3.860$ Å, $b = 3.860$ Å, $c = 11.813 \pm 0.001$ Å)

h	k	l	d_o (Å)	d_c (Å)	I/I_0
0	0	3	3.929	3.925	9
1	0	0	3.852	3.848	7
1	0	2	3.229	3.223	14
1	0	3	2.749	2.750	100
1	1	0	2.725	2.723	58
1	1	2	2.475	2.473	4
0	0	5	2.358	2.358	12
1	0	4	2.342	2.341	19
1	1	3	2.240	2.239	19
0	0	6	1.9665	1.9661	11
2	0	0	1.9275	1.9272	41
1	1	5	1.7838	1.7841	9
2	0	3	1.7307	1.7309	4
2	1	0	1.7247	1.7241	5
0	0	7	1.6862	1.6857	6
2	1	2	1.6554	1.6550	6
1	1	6	1.5949	1.5951	17
2	1	3	1.5792	1.5793	51
1	0	7	1.5441	1.5447	5
2	0	5	1.4946	1.4932	10
2	1	4	1.4881	1.4889	14
1	1	7	1.4338	1.4342	5
2	0	6	1.3768	1.3771	15
2	2	0	1.3635	1.3636	15
2	0	7	1.2691	1.2695	5
3	0	3	1.2211	1.2222	17
2	1	7	1.2060	1.2060	5

TABLE 4

Observed and calculated interplanar spacings for the $BaCuO_2$ phase (cubic structure, space group Im^3m [19], lattice parameter $a = 18.295 \pm 005$ Å)

h	k	l	d_o (Å)	d_c (Å)	I/I_0
5	2	1	3.345	3.345	11
4	4	0	3.238	3.239	14
5	3	0	3.142	3.142	77
4	3	3	3.143	3.142	
4	4	2	3.053	3.053	100
6	0	0	3.053	3.053	
5	3	2	2.969	2.972	60
6	1	1	2.969	2.972	
6	2	0	2.903	2.896	7
6	3	1	2.698	2.700	3
4	4	4	2.644	2.644	27
7	1	0	2.592	2.590	10
5	4	3	2.592	2.590	
5	5	0	2.592	2.590	
6	4	0	2.539	2.540	3
7	2	1	2.491	2.492	13
6	3	3	2.491	2.492	
5	5	2	2.491	2.492	
6	4	2	2.452	2.447	2
7	3	0	2.404	2.405	8
7	3	2	2.324	2.323	19
6	5	1	2.324	2.323	
8	0	0	2.290	2.289	13
8	1	1	2.254	2.254	29
7	4	1	2.254	2.254	
5	5	4	2.254	2.254	
6	4	4	2.222	2.221	6
8	2	0	2.222	2.221	
6	5	3	2.185	2.188	1
8	2	2	2.158	2.158	31
6	6	0	2.158	2.158	
7	5	0	2.129	2.129	11
8	3	1	2.129	2.129	
7	4	3	2.129	2.129	
6	6	2	2.098	2.100	30
7	5	2	2.074	2.073	12
8	4	0	2.047	2.047	8
9	1	0	2.021	2.022	3
8	4	2	1.9955	1.9977	2
9	2	1	1.9750	1.9743	10
7	6	1	1.9750	1.9743	
6	5	5	1.9750	1.9743	
6	6	4	1.9529	1.9517	1

TABLE 4 (continued)

h	k	l	d_o (Å)	d_c (Å)	I/I_0
7	5	4	1.9294	1.9299	17
8	5	1	1.9294	1.9299	
9	3	0	1.9294	1.9299	
9	3	2	1.8861	1.8883	5
7	6	3	1.8861	1.8883	
8	5	3	1.8501	1.8494	30
9	4	1	1.8501	1.8494	
7	7	0	1.8501	1.8494	
7	7	2	1.8122	1.8127	9
10	1	1	1.8122	1.8127	
10	2	0	1.7952	1.7952	1
8	6	2	1.7952	1.7952	
9	5	0	1.7776	1.7781	14
9	4	3	1.7776	1.7781	
10	2	2	1.7601	1.7616	4
6	6	6	1.7601	1.7616	
10	3	1	1.7461	1.7455	8
7	6	5	1.7461	1.7455	
9	5	2	1.7461	1.7455	
8	5	5	1.7142	1.7146	6
8	6	4	1.6995	1.6997	5
9	6	1	1.6851	1.6852	7
10	3	3	1.6851	1.6852	
11	1	0	1.6570	1.6573	2
9	5	4	1.6570	1.6573	
8	7	3	1.6570	1.6573	
9	6	3	1.6300	1.6308	6
11	2	1	1.6300	1.6308	
10	5	1	1.6300	1.6308	
8	8	0	1.6182	1.6180	3
11	3	0	1.6053	1.6055	2
9	7	0	1.6053	1.6055	
8	8	2	1.5965	1.5933	1
10	4	4	1.5965	1.5933	
11	3	2	1.5814	1.5813	17
9	7	2	1.5814	1.5813	
7	7	6	1.5814	1.5813	
8	7	5	1.5583	1.5582	7
11	4	1	1.5583	1.5582	

DTA measurements

A commercial Netzsch apparatus equipped with a quantitative DDK measuring head, with platinum crucibles as specimen holders, was used for

TABLE 5

Observed interplanar spacings for the X_1 phase ≡ Cu_2O [20]

d (Å)	I/I_0	$d(Cu_2O)$ (Å)
2.938	10	3.02
2.874	20	–
2.703	9	–
2.467	100	2.47
2.139	32	2.14
1.704	7	–

the determination of the temperature changes of processes occurring within the range 20–1350 °C. The temperature was measured by an independent Pt–PtRh10 thermocouple calibrated by ICTA NBS standard set. The temperature difference ΔT was indicated by a differential Pt–PtRh10 thermo-

TABLE 6

Observed interplanar spacings for the X_2 phase

d (Å)	I/I_0
3.165	22
3.105	29
3.001	70
2.938	100
2.901	80
2.874	48
2.794	30
2.745	25
2.561	14
2.492	78
2.411	10
2.309	8
2.279	9
2.098	22
1.9529	9
1.9298	10
1.9017	23
1.8909	25
1.8227	9
1.7735	5
1.7077	28
1.6957	15
1.6617	10
1.6135	13
1.5819	23
1.5747	20

couple and was recorded with a sensitivity of 0.33 K cm^{-1} at 1000 °C. The heating rate employed was 5 K min^{-1}. All the measurements were carried out on samples of 100 mg in an oxygen atmosphere.

X-ray analysis

An X-ray diffractometer (DRON-III) using nickel-filtered Cu $K\alpha$ radiation was employed for phase analysis of the prepared samples.

RESULTS

The data on the individual phases which were found in the region investigated are summarized in Tables 1–8 with emphasis on the intensity of diffraction lines. The phases 1 : 0 : 1, 2 : 1 : 1 and 1 : 2 : 3 were well characterized, but the X_1, X_2, X_3 and X_4 phases were far from clear. The compositions of these phases could not be determined from the X-ray diffraction spectra. A serious problem was the possible contamination by platinum ions arising from the corrosion of the platinum sample holders. In the samples with the starting compositions 1 : 1 : 2, 1 : 2 : 3 and 1 : 4 : 5 heated above 1075 °C a phase containing platinum was found; this is shown in

TABLE 7

Observed interplanar spacings for the X_3 phase

d (Å)	I/I_0
3.243	42
2.915	100
2.659	5
2.489	5
2.353	10
2.326	10
2.166	26
2.132	18
2.119	12
2.084	7
1.9513	10
1.9046	1
1.8292	6
1.7371	16
1.7098	7
1.6237	15
1.4807	4
1.4547	16
1.4167	9

TABLE 8

Observed interplanar spacings for the X_4 phase

d (Å)	I/I_0
4.087	13
3.544	13
3.427	22
3.166	17
3.020	28
2.986	83
2.863	100
2.774	36
2.756	23
2.702	53
2.640	17
2.600	17
2.554	25
2.491	28
2.467	18
2.437	17
2.395	13
2.372	13
2.263	23
2.095	50
2.079	43
2.034	17
2.022	47
2.002	13
1.940	17
1.903	27
1.891	15
1.835	27
1.762	27
1.712	25
1.698	43
1.653	15
1.560	18
1.554	12

Fig. 1. The microprobe composition analysis of this single phase revealed the $Y_{20}Ba_{60}Cu_{13}Pt_{17}O_{77}$ stoichiometry, roughly corresponding to the simple stoichiometry 1 : 3 : 1 if Pt substitutes for Cu. The preparation of the 1 : 3 : 1 phase was not successful; this phase was indicated in our experiments on the quenching of 1 : 2 : 3 melts [21], where Pt contamination was not detected.

In order to determine the phase relations we treated individual samples at various temperatures and analysed the phases present in the quenched-in state. The results are listed in Table 9. The parentheses indicate phases

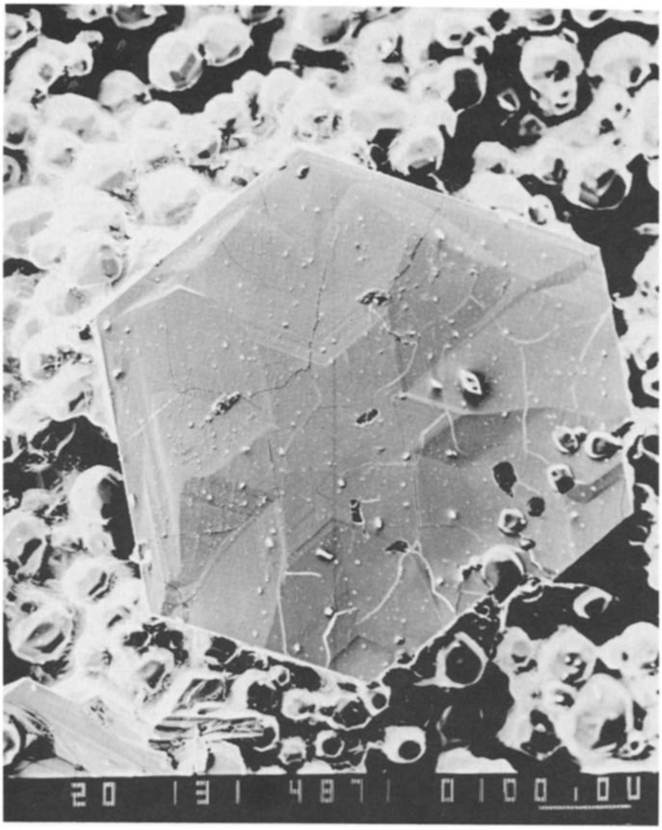

Fig. 1. Electron micrograph of the $Y_{20}Ba_{60}Cu_3Pt_{17}O_{77}$ phase.

which formed probably as a result of an insufficient cooling rate for preserving the high-temperature state.

DTA measurements were carried out on samples in various states (from calcinated oxide mixtures to quenched samples). To evaluate the thermal processes occurring in the samples we also measured pure binary or ternary compounds. The DTA effects obtained (mainly simple and well distinguished) were related to the peritectic temperatures as shown in Table 10.

DISCUSSION

We attempted to draw a pseudobinary phase diagram along the 1 : 0 : 1–0 : 1 : 1 line using both the X-ray analysis and DTA data given above. Before going into detail, the following possible sources of misinformation need to be listed:

(i) change in starting composition owing to platinum contamination;
(ii) reactions distorting the high-temperature state during quenching;

TABLE 9

Results from X-ray phase analysis of quenched samples

$YO_{1.5}$: BaO : CuO	925 ° C	950 ° C	975 ° C	1050 ° C	1100 ° C	1150 ° C	1200 ° C
1 : 0 : 1	$YCuO_{2.5}$	$YCuO_{2.5}$	$YCuO_{2.5}$	$YCuO_{2.5}$	$YCuO_{2.5}$	$YCuO_{2.5}$	–
12 : 1 : 13	Y_2BaCuO_5 $YCuO_{2.5}$ CuO	Y_2BaCuO_5 $YCuO_{2.5}$ CuO	Y_2BaCuO_5 $YCuO_{2.5}$ CuO	Y_2BaCuO_5 $YCuO_{2.5}$ CuO	$YCuO_{2.5}$ Y_2O_3 (CuO)	$YCuO_{2.5}$ Y_2O_3 (CuO)	X_1 Y_2O_3 (CuO)
5 : 1 : 6	Y_2BaCuO_5 $YCuO_{2.5}$ CuO	Y_2BaCuO_5 $YCuO_{2.5}$ CuO	Y_2BaCuO_5 $YCuO_{2.5}$ CuO	Y_2CuO_5 $YCuO_{2.5}$ CuO	$YCuO_{2.5}$ Y_2O_3 (CuO)	X_1 Y_2O_3 (CuO)	X_1 Y_2O_3 (CuO)
2 : 1 : 3	Y_2BaCuO_5 CuO	Y_2BaCuO_5 CuO	Y_2BaCuO_5 CuO	$(YCuO_{2.5})$ Y_2O_3 CuO	X_2 Y_2O_3 (CuO)	X_2 Y_2O_3 (CuO)	(X_2) Y_2O_3 (CuO)
4 : 3 : 7	–	–	–	–	$X_2 + (Y_2BaCuO)$ Y_2O_3 (CuO)	X_2 Y_2O_3 (CuO)	–

1:1:2	$YBa_2Cu_3O_{6.5}$ Y_2BaCuO_5 CuO	$YBa_2Cu_3O_{6.5}$ Y_2BaCuO_5 CuO	$YBa_2Cu_3O_{6.5}$ Y_2BaCuO_5 CuO	Y_2BaCuO_5 CuO	Y_2BaCuO_5 (X_2) (CuO)	Y_2BaCuO_5 (X_2) (CuO)	X_2 Y_2O_3 (CuO)
1:2:3	$YBa_2Cu_3O_{6.5}$	$YBa_2Cu_3O_{6.5}$	$YBa_2Cu_3O_{6.5}$	Y_2BaCuO_5 CuO	Y_2BaCuO_5 (X_2) (CuO)	Y_2BaCuO_5 X_3 (CuO)	Y_2BaCuO_5 X_2 (CuO)
1:4:5	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	Y_2BaCuO_5 CuO	X_3 X_4 CuO	Y_2BaCuO_5 X_2 CuO	Y_2BaCuO_5 X_2 CuO
1:6:7	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	Y_2BaCuO_5 CuO	X_3 X_4 CuO	–	–
1:12:13	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	$YBa_2Cu_3O_{6.5}$ $BaCuO_2$	X_3 X_4 CuO	X_3 X_4 CuO	–	–
0:1:1	$BaCuO_2$	$BaCuO_2$	–	–	–	–	–

TABLE 10

Peritectic or melting temperatures of the individual phases which exist in the $YCuO_{2.5}$–$BaCuO_2$ system

Compound	Sintering temperature (° C)	Peritectic or melting temperature (° C)
CuO	–	1076
$BaCuO_2$	950	1025
$YCuO_{2.5}$	1125	1177
Y_2BaCuO_5	1125	1285
$YBa_2Cu_3O_{6.5}$	950	1000

(iii) oxygen non-stoichiometry;

(iv) reaction hysteresis during DTA measurements arising from non-equilibrium conditions.

As a result we were unable to construct the phase diagram accurately within the entire temperature region investigated. Therefore in the proposed phase diagram (see Fig. 2) we have distinguished between the certain phase boundary lines (full lines) and those which are only approximate (broken lines). The points included correspond to the enthalpy changes observed by

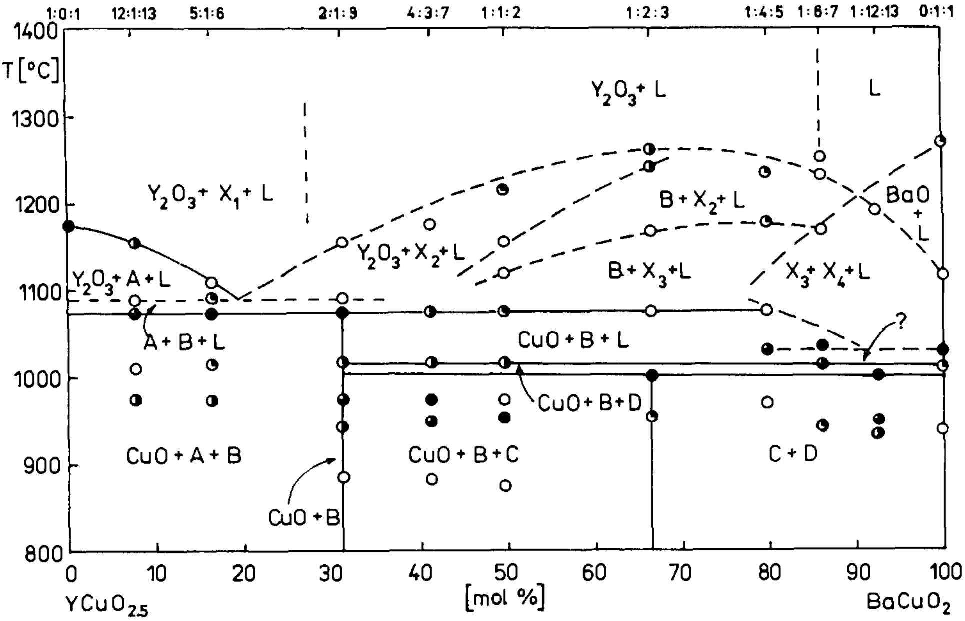

Fig. 2. Pseudobinary phase diagram of the $YCuO_{2.5}$–$BaCuO_2$ system: full line, determined boundary; broken line, estimated boundary. Known phases: A, $YCuO_{2.5}$; B, Y_2BaCuO_5; C, $YBa_2Cu_3O_{6.5}$; D, $BaCuO_2$. Unknown phases: X_1, X_2, X_3, X_4. Circles represent amount of heat accompanying the DTA endothermic effects: ○, smallest enthalpy change; ◔, 25%; ◑, 50%; ◕, 75%; ●, largest enthalpy change.

DTA, given in the sequence of their magnitude, from filled circles (largest enthalpy change) to half-filled circles to open circles (smallest enthalpy change).

The low temperature region (below 1075 °C) seems to be reliable enough, although we could not associate some DTA effects observed at temperatures below 975 °C. X-ray analysis of the samples in question showed non-substantial changes.

The phases which coexist in the lower temperature region are as follows: 1 : 0 : 1 + 2 : 1 : 1 + CuO for 0–33.3 mol.% of 0 : 1 : 1, 2 : 1 : 1 + 1 : 2 : 3 + CuO for 33.3–66.6 mol.% of 0 : 1 : 1 and 1 : 2 : 3 + 0 : 2 : 1 for 66.6–100 mol.% of 0 : 1 : 1. The peritectic decomposition of the 1 : 2 : 3 phase at 1000 °C and of $BaCuO_2$ at 1025 °C leads to the formation of 2 : 1 : 1 + 0 : 1 : 1 + CuO in the narrow range 1000–1025 °C, 2 : 1 : 1 + CuO + liquid phase in the range 1025–1075 °C and to the X_3 and X_4 phases. Above 1075 °C the situation becomes more complicated owing to the formation of liquid phases where the Y_2O_3, 1 : 0 : 1, X_1, X_2, X_3 and X_4 phases coexist. Thus only the boundary between the region Y_2O_3 + 1 : 0 : 1 + liquid and Y_2O_3 + X_1 + liquid for the concentration range 0–19 mol.% of 1 : 0 : 1 was successfully determined.

The BaO-rich (right-hand) side of the phase diagram (see Fig. 2) is less reliable than that of the $YO_{1.5}$-rich side owing to the platinum inserted during sample preparation. The higher the BaO content the more probable it is that sample contamination will occur (Fig. 1). We found it difficult to make an alternative choice of material for the sample holder owing to the low melting temperature (Au,Cu), oxidation (Mo,W) and/or reactivity during prolonged firing (oxides). The problems of contamination and the uncertainty inherent in the sample quenching made the resolution of the high temperature boundary extremely difficult. Therefore we could not identify the proposed phase boundaries exactly. Further simplification was introduced when we assumed that Cu ions were present only as Cu^{2+} and when the deviations from stoichiometry were neglected.

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