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BINARY AND TERNARY COMPOUNDS, PHASE DIAGRAMS AND CONTAMINATIONS IN THE $YO_{1.5}$-BaO-CuO SYSTEM AUXILIARY TO SUPERCONDUCTING CERAMICS

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ABSTRACT

The binary phases and compatibilities of the BaO-CuO, $YO_{1.5}$-BaO and $YO_{1.5}$-CuO systems are discussed. The different variants of $YBa_2Cu_3O_{7-y}$ are shown in dependence on y. So far reported existence of the ternary compounds (in the ratio Y:Ba:Cu) 1:3:2, 1:4:3, 1::2:4, 1:5:3, 3:8:5, 2:3:5 and 1:4:2 are questioned. The ternary phase diagram and pseudobinary cuts of the $YCuO_{2.5}$-(1:2:3)-$BaCuO_2$ and $Y_5BaO_{8.5}$-(1:2:3-2:1:1)-$Ba_3Cu_5O_8$ are reviewed. The distorting effect of impurities from air (e.g. oxycarbonates formation) and/or from the sample holder (e.g. Pt-substituted compounds) is analysed. On basis of the 1:2:3 structural model hypothetical superconducting compounds 1:1:2, 1:3:4 and 1:2:4 are predicted assuming double layers of corner-sharing square-planar CuO_4 units.

INTRODUCTION

Since the 1987 pioneering discovery of high temperature superconductors (HTS), over 5000 relevant reports have been published which are almost impossible to review (see recent survey articles [1-5]). Technical applicability of HTS is for the moment difficult because of certain metastability of this kind of ceramic material in long-term practical utilization. Although known for thousands of years, ceramic materials in general are still far from being fully understood owing to interfacial phenomena and heterogeneity of multicomponent systems. Nevertheless the basic approach includes the classical search for phase diagrams and indentification of compounds responsible for specific properties of the system investigated.

In this respect no systematic study of all the phase compatibility relations in the Y-Ba-Cu-O-(R) system have been reported. Limited information is available in the American Ceramic Society compilations (only on binary phase diagrams) and only a few laboratories are more intensively engaged in this study. These are for example the U.S. National Bureau of Standards in Gaithersburg or IBM of Yorktown Height in New York, the Italian Institute of Physical Chemistry of Genova University or the MASPEC Institute of Parma and last but not least our Institute of Physics in Prague .

The aim of this survey is to list and to discuss the available data on phase relations within the $YO_{1.5}$-BaO-CuO system. For the sake of simplicity the compositions are abbreviated by the stoichiometric numbers **Y:B:C** in the formulae $Y_YBa_BCu_CO_X$ (regardless of the value of X) traditionally maintaining the perovskite formulae (Ba substituted for Y).

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TECHNOLOGICAL PROCEDURES AND CRYSTALCHEMISTRY OF THE SAMPLE

Since processing conditions essentially affect the final properties of HTS great interest has been generated in **$YBa_2Cu_3O_{7-y}$** (i.e. the 123 composition) as the point component. Like most non-stoichiometric materials lying near a metal-insulator instability the superconductive 123 may tend to phase separate and can exist in several modifications. The first phase diagrams [6,7] were thus directed to cover existence areas of the superconduting 123 with respect to its oxygen content y [1,8-11], see Fig.1.

The serious problem found on sintering of such types of materials has been connected with grain surfaces being seemingly different from the bulk. The liquid phase is often noticed along the grain boundaries where it can accelerate the grain growth. The liquid formation, however, can occur locally just for areas which are slightly rare-earth poor although not heated above the required sintering temperature of about 950°C. While the liquid phase formation can generally be used to enhance densification it is also known to be a problem possibly leading to poorer superconductivity. Amorphous regions are also reported to appear on the grain surfaces [12]. They are due to reactions with H_2O and/or CO_2 or due to disordering processes induced by the crushing and prolonged grinding procedures used to prepare samples either for sintering or for observations (e.g. microscopy). It is also known that some originally well-accepted dopants can later segregate on the grain surfaces as the case of sulphur to form outer layers of $BaSO_4$ [13]. In addition it is difficult to prevent the existence of unwanted impurity phases due to incomplete reactions of feed mixtures (e.g. popular $BaCO_3$ which can even be formed by phase separation from well prereacted $BaCO_3$-free mixtures upon reaction with air and which we could even detect in some melts). The parasitic reactions with CO_2 in air or with material of the sample holder or temperature detector should be considered. For example the basic 123 composition reacts with most crucible materials including silica, alumina and platinum. Zirconia, single-crystals of MgO, gold and particularly Pd-Ag alloys are relatively inert. Highly reactive starting mixtures (containing e.g. $Ba(OH)_2$ or BaO_2) chosen to accelerate sintering due to early liquid formation [14] (e.g. in the region of 80 - 450°C) also increase the agressivity towards the noble metals. Precursor methods using e.g. coprecipitated oxalates can distort presumed stoichiometry [14]. The best method to decrease the sample reactivity with platinum appears to be the use of prereacted pseudobinary oxides such as $BaCu_3O_4$ (i.e.013) or $BaCu_4O_5$ (014) [15] or directly the 211. The ideal sample holder is evidently the one made from the presintered 123. Alternatively one can use the powder beds protecting the pellets from reacting with the crucible material and possibly from the loss or gain of volatile species. In this respect the melt soaking experiments [35] proved useful to solve phase coexistence. Extracting the liquid phase formed into the sample supporting porous bed makes it possible to analyse the sample composition by the ordinary lever rule [16].

Another problem is the homogeneity of the microcrystalline samples. The repeated grinding, milling, pressing and firing of a feed mixture may not guarantee the completeness of solid-state reactions to occur during sintering. The near equilibrium state should be best approached by simultaneous treatments from below and from above the required temperatures, if possible. Intimate mixing of starting components (even down to the molecular level) is preferable although not always satisfactory. Too short and/or too long firing may result in the formation of intermediate com-

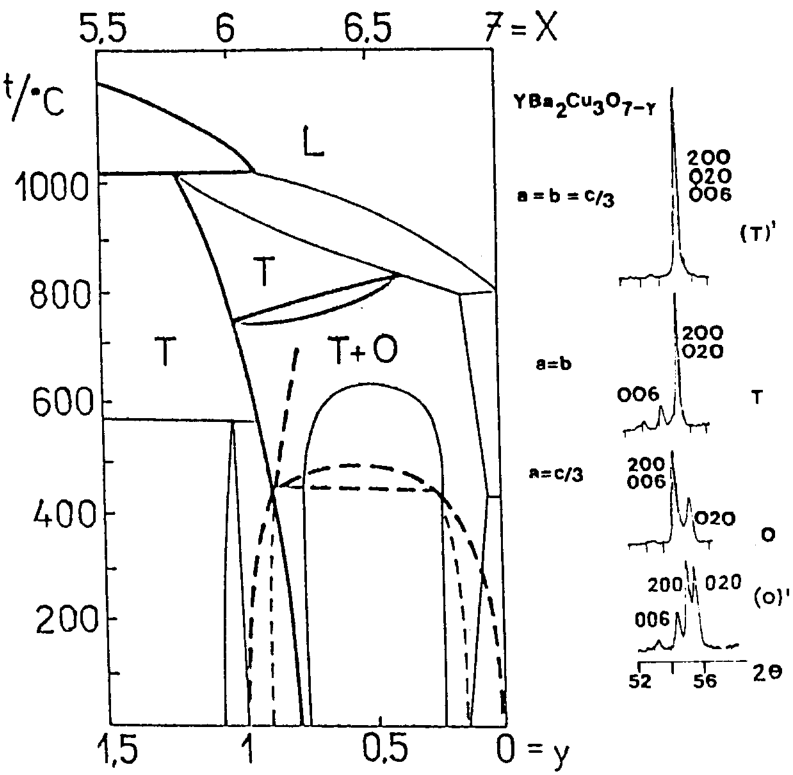


FIG. 1: The pseudobinary phase diagram proposed by Hauck et al [6] on the basis of TG measurements (solid lines) with the inserted data calculated by Khachaturyan et al [7] (dotted lines) showing the O-T order-disorder transformation and solvus lines (bold) as well as the spinodal instabilities. It is evident that the existence regions are not clear as yet because various modifications of the 123 phase reported in [8-10] are not included (though the O` phase was already considered in [7]) ; compare the following table:

Struct.	Lattice paramet.			y	Lat.specif.	Preparation cond.
O [8]	3.881	3.852	11.602	--	c/b>3,c/a<3	$p_{O_2} \simeq 10$atm or BaO_2
O [8]	3.888	3.826	11.677	--	c/b>3,c/a≃3	T<1000°C,cooling
O [9]	3.886	3.832	11.680	-0.06	b<a≃c/3	--
O`[9]	3.871	3.385	11.751	-0.47	b<a<c/3	cycling in air
T [8]	3.857	--	11.833	--	c/a>3	T>1000°C,from melts
T [11]	3.860	--	11.813	--	c/a>3	quenched from 950°C
T [8]	3.872	--	11.615	--	c/a≃3	--
T [9]	3.855	--	11.810	-0.89	a=b<c/3	--
T`[9]	3.877	--	11.643	+0.05	a=b=c/3	this phase is called "pseudocubic" and was prepared by mechanical activation [9,10] (intensive milling) followed by annealing (750°C).Its characteristic x-ray lines are shown at the right side in comparison with the T,O and O`phases (hkl values marked, CoK_α radiation).

pounds (usually enhanced by uneven mixing) and/or in the separation of metastable states (often supported by parasitic reactions), respectively. These phenomena became very important for such observations which are carried out during heating or cooling (e.g. popular and easily accessible DTA). Resulting data, however, can bear nonnegligible degree of distortion due to hysteresis inherent in the transformations investigated. Neglecting undesired inhomogeneities often reported at the microscopic level the energy dispersive x-ray analysis exhibited uniform distribution of cations down to the limit of resolution (or 1 μm) presumably for well reacted samples. However, higher resolution studies showed chemical inhomogeneities at the 0.05 μm scale. There appears to be some degree of decomposition even for the well prepared (single phased) compounds sometimes within a single 1 μm particle to further (usually Ba-Cu rich) phases. Spectroscopic measurements revealed a certain content of carbon and oxygen associated with the -CO and -OH groups mainly localised in the grain surface layers. All this complicates the phase analysis and often leads to controversial results.

BINARY COMPOUNDS AND PHASE DIAGRAMS

The known compounds include the end member oxides and the additionally discussed binary compounds so far reported:

(i) In the **BaO-CuO system** the barium cuprate 011 has already been described by Midgeon et al [17] and recently reported by Roth et al [18] to melt incongruently between 1010 and 1020 °C. Frase et al [19] included the additional binary compounds 021 and 031. The compound 021 was identified by Wong-Ng et al [20], Deleeuw et al [22] and Wang et al [21]. It decomposes above 850 °C [19] and partly melts at about 950 °C [18]. The 031 compound was not confirmed [22, 23] but the composition 035 showed to be a compound [22] stable up to 800 °C presumably formed during the 123 synthesis at low firing temperatures when starting from peroxides or nitrate precursors [22]. Hermann and Zhang [15] rather advocated **starting** from the composition 013 and 014. Roth et al [23] obtained a single phase material from BaO_2 and CuO mixtures in the 4:1 and 6:1 ratio heated up to 900 °C in O_2. The eutectic between 011 and CuO was estimated slightly above 900 °C at about 38 mol% BaO while Nevřiva et al [24] and Licci et al [25] found the eutectic point at 925 °C with 28 mol% BaO.

The discrepancy between the reported values can possibly be caused by various materials used as the sample holder presumably due to the formation of an intermediate phase Ba_4PtO_6 [24]. Similar phase was also reported by Bykov et al [55] during the growth of single crystals having the stoichiometry $Ba_4(Cu,Pt)O_6$. The existence of the 012 compound was not confirmed [23] in the quenched melts from the recommended temperature of about 1200 °C but it was shown [26] that some unknown cubic and/or orthorhombic phases can be detected.

(ii) The **BaO-$YO_{1.5}$ phase diagram** was reported by Lopato et al [27] at temperatures above 1200 °C and in further studies by Kwestroo et al [28] at lower temperatures. Two compounds 210 and 430 exist [27-30], the 210 being stable up to 1400 °C and the 430 melting incongruently at 2160 °C. New (possibly metastable) compounds were found with the stoichiometry 110, 120 and 430. DeLeeuw et al [22] did not succeed to prepare these phases from BaO2 but the 120 could be made at about 1000 °C starting from $BaCO_3$. The carbon content measurements imply that 120 is rather an oxycarbonate with the composition $Ba_4Y_2O_7.CO_2$ exhibiting a tetragonal unit cell. This is in accordance with the data by DeLeeuw et al [22] and Costa et al [29] reporting oxycarbonates (120).CO_2 and (110).CO_2 . It was shown [29] that the orthorhombic 210 decomposes peritectically at about 1030 °C to the 430.

(iii) A preliminary phase diagram of the **$YO_{1.5}$-CuO system** was published by Roth et al [18]. The major orthorhombic compound is the yttrium cuprate 101 determined previously by Lambert [31] to melt incongruently between 1150-1180 °C. Nevřiva et al [24] reported the eutectic temperature 1075 °C with about 7.5 mol% $YO_{1.5}$. Two other forms were reported: the reduced $YCuO_2$ [32] (prepared under p_{O2}~10^3 Pa) and the oxidized $YCuO_3$ [33] (p_{O2}~10^7 Pa) both of them, however, not being detected in the current studies of Y-Ba-Cu-O phase equilibria.

The compiled shapes of the respective binary phase diagrams are collectively shown in Fig.2 (including data by Gadala et al [34] on the CuO-Cu_2O phase equilibria). All diagrams shown herewith are based on the averaged data received using both convenient atmospheres (i.e. air and flowing O_2) as the position differences of characteristic points and lines lie within experimental errors.

TERNARY COMPOUNDS AND PHASE COMPATIBILITIES

The preliminary published diagrams [1,18,19,21,35,36] showed the existence of three basic ternary compounds:

(i) **The 211 compound** initially reported by Michel and Raveau [37] as the insulating green phase to crystallize in an orthorhombic unit cell (space group P6nm, a=7.132,b=12,181 and c=5.685 Å).

(ii) **The 123 compound** was identified as a bulk superconductor existing in a low-temperature orthorhombic (Pmmm) and in a high-temperature tetragonal (P4/mmm) modification. The occurrence of different variants of the 123 and the temperature induced O-T phase transformation [1-5] are strong indications for the important role of the oxygen vacancy ordering, cf. Fig.1.

(iii) **The 132 compound** (e.g.[35]) is often called the other perovskite (P4mm ,a= 4.07 and c= 4.01 Å), however, its existence is not as yet clear [1,11,18,23].

In the early literature there were reported various additional ternary compounds such as the orthorhombic 213 [38] which probably does not exist either. In addition **the 142 phase** was found to occur in the tetragonal and cubic forms [39, 40] and it is supposed to be another superconducting compound as well as the recently reported **124 phase** [61].

Let us discuss some very recent results. Roth et al [23] prepared a series of samples with the nominal formulae 0.8:3.2:2-x where x varied from 0.1 to 0.4 (i.e. to the 142). Specimens from x=0.1 to 0.3 were single phased. Although bearing some similarity with the 132 they were rather a solid solution somewhere along the section 132-142-153. However, the existence of the 142 was not excluded.

DeLeeuw et al [22] reported the identification of new compounds 143,385 and 152. The pseudocubic (a= 8.069 Å) or tetragonal (P4/mmm, a= 8.069, c=4.035 Å) 143 was prepared by firing the intimate mixture of $Ba(NO_3)_2$ (or BaO_2) with Y and Cu oxides at 950 °C in air. However, the 143 phase was not produced when using $BaCO_3$ in the feed mixture. The 385 phase is assumed [22] to be the ordered modification of the 132 [19] and was obtained by firing the Y and Cu oxide mixture with $BaCO_3$ above 950 °C. It exhibits the tetragonal unit cell (P4/mmm, a= 5.788 and c= 8.014 Å). The 152 compound was identified as a single ordered phase of the 143 crystallizing in the orthorhombic unit cell (Immm, a= 4.03, b= 4.09 and c= 21.6 Å). Here we should note the article by Kostcheeva et al

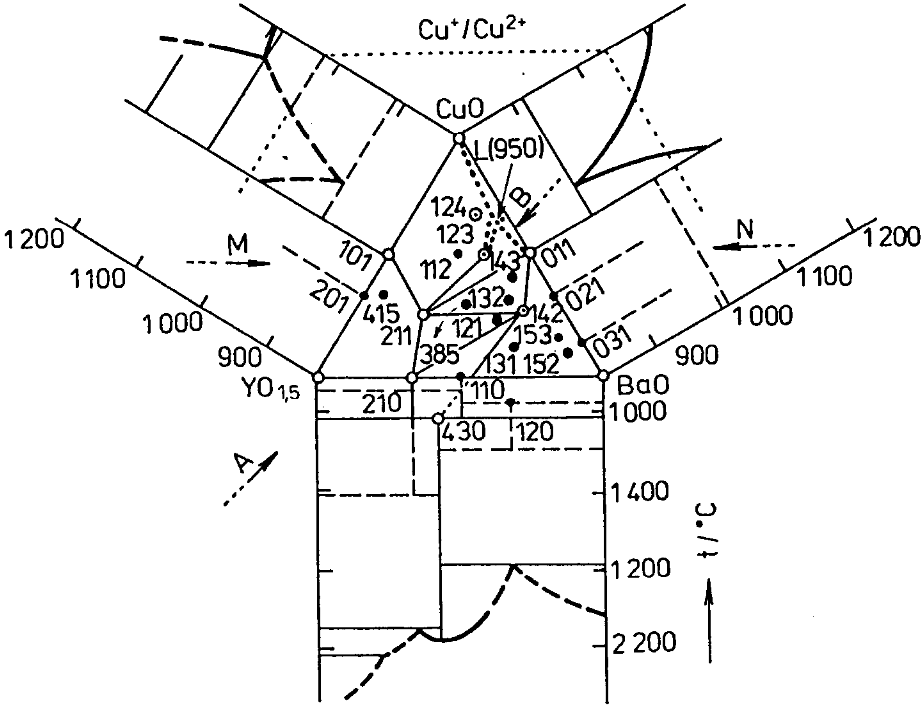


FIG. 2.: The ternary phase diagram with the proposed tie lines thought to exist at about 950 °C. The corresponding binary phase diagrams are also included, the dotted lines showing still questionable boundaries. The stable, superconductive and metastable compounds are illustrated by open, dotted and small solid circles , respectively.

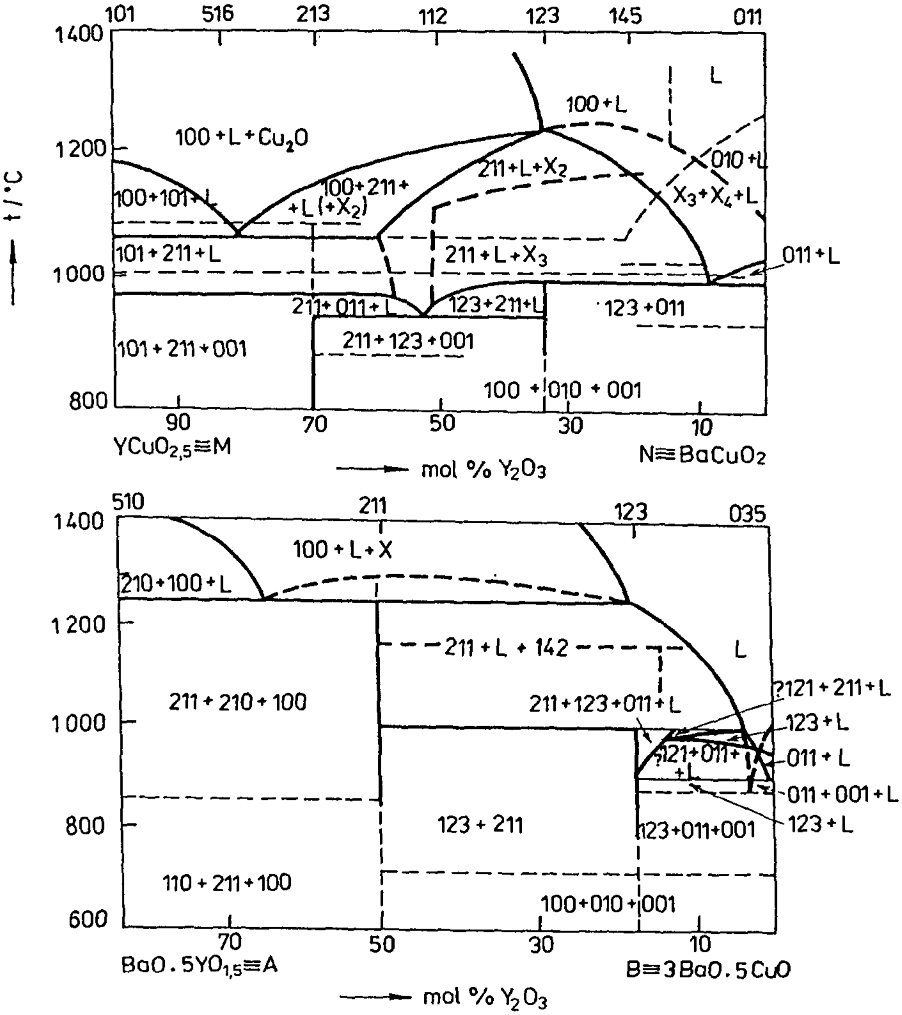


FIG. 3.: The tentative pseudobinary cuts of the 101-123-011 [11,23] and of the 510-211-123-035 [23,36,40] jointly drawn on the basis of various sources of experiemntal data. The question marks at not yet mentioned phase 121 (right bottom) inserted according to [23] indicate uncertainty as the existence of the 142 phase may be equally possible. Neither the 142 phase nor these regions are as yet clear enough.

[54] who reported yet another orthorhombic phase 153 (Pmmm).

The existence of the 143 was not substantiated [23] and Roth et al strongly suggested that many of these other perovskite phases are chemically and physically **oxycarbonates**. In our studies [40,41] we also originally assumed the existence of the 143 which later turned out to be a heavily contaminated "131" phase, Cu being replaced by Pt dissolved from the sample holder [11]. We, did not succeed, however, in preparing the 131 phase as a single pure compound nor did we find the 143. Šesták et al [41] found upon quenching the 123 melts an unidentified phase but different from that reported by McKittric etal [42] prepared under comparable conditions of severe freeze-in of a high-temperature state [44].

Yet another phase of the rough stoichiometry 235 can be deduced from the article by Matsuzaki et al [43]. A phase of the composition $Y_{2-x}Ba_xCu_2O_{5-x/2}$ was identified for a very small x to have an identical x-ray pattern with the 101 compound but different intensities [9,10] (abbreviated "101").

All the above discussed phases are listed in Table I in order to compare their interplanar spacing and relative intensities. It follows that there is some coincidence of the major d-values (e.g. the 235 and the tetragonal 123 for 0.270 or the 132,385,152 and 142 for 0.287 as well as the Pt-substituted "131" and "123" for 0.323 and 0.290). To complete the comparison the diffraction lines of some unidentified phases are included as detected in the as-quenched samples obtained under different cooling rates of the 123 melts. Prevailing diversities, however, make further analysis too difficult to shed more light on the existence of individual phases.

TERNARY PHASE DIAGRAM AND PSEUDOBINARY CUTS.

So far the published ternary phase diagrams [1,18,19,21,23,35, 36,45,46,58,59,60] often indicate tie lines between phases and also solid solutions. It should be pointed out that the exact position of tie lines would still require more intensive investigation and so it is possible that future research will result in certain modifications. A sketch of primary phase fields was recently shown by Roth et al [23]. A more detailed calculation on primary crystallization in the 001-011-211 triangle was introduced by Nevriva et al [16] as based on a separation of melt from a fired sample and the consequent analysis of its solid residue. The possible binary and ternary phases and presumed tie lines are collectively indicated in Fig.2.

The temperature-composition cuts through this ternary system were in the center of interest to include the point component 123. The **system 101-123-011** is one of the most intensively studied cut although being non-binary as originally noticed in earlier papers [18,19,21]. The system is intersected by the pseudobinary joint between the 211 and 001 where the sample melting (in air) proceeds in three steps [23], congruently at 930°C (53mol% 100; 211+123+011), incongruently at 960°C (60mol% 100; 211+101+011+001) and both congruently (10mol% 100; 100+123+011) and incongruently (33mol% 100; 211+123+011+001) at 1002°C. Working in oxygen our results revealed only two clear invariant points at 999°C (34mol% 100; 211+123+011+001) and at 1015 and 1070°C (70mol% 100; 211+011+101+001), cf. Fig. 3. Roth et al [23] showed in more detail the melting behaviour of the 123 through a four-phase region assuming a significant activity of CO_2 in two or more of these phases. From the failure to synthesize the 123 compound below 750 °C combined with the apparent loss of crystallinity at highly pro-

Table I : ESTIMATE OF THE MAJOR DIFFRACTION LINES OF SOME REPORTED PSEUDOTERNARY PHASES STILL IN QUESTION.

d-value	132	143	385	152	235	quenched 123		sintered 142		"131"	"123"	"101"
+0.0015	[35]	[22]	[22]	[22]	[43]	10^3K/s	10^4K/s	tetra.	cubic	[11]	[50]	[10]
0.392					xx							
0.366						x						
0.323										xxx	xxx	
0.312							xx					
0.297				xxxx								
0.294				xxxx								
0.290			xx			xxx	x	xx		xxxx	xxxx	
0.287	xxx		xxxx	xxxx			xxx	xxx	xxx			
0.285	xxxx	xxxx										x
0.275					xxxx							
0.270												xxxx
0.247							xxx					
0.234	x		x					xx	xx	x		
0.224				x	xx							
0.218										xx		
0.215			x								xx	
0.212											x	
0.204	xx						xx	x	xx			
0.202		x									x	x
0.195					xx							
0.189						x	xx					x
0.173				x								
0.168				x		xx		xx		xx		
0.166		x	x	x		x	x	x	x			
0.158					xx		xx					
0.145											x	
0.127		x										

Intensities are abbreviated as follows: xxxx = 100-80 %, xxx = 80-60 %, xx = 60-40 % and x = 40-20 % .

"YBC" indicates a substituted phase YBC using the simplified atomic ratio Y:Ba:Cu.

longed annealing (700 °C and 1700 hrs) they concluded [23] that the T-O transformation bears rather a metastable character.

A very important cut is the one between the compositions **$BaO.5YO_{1.5}$ and 3BaO.5CuO** since it includes the two main compounds 211 and 123 as well as the possibly primary phase field for the superconductor formation suggested in [18,23,36,40,59-61]. Here the solidus appears [23] to occur at about 910 °C in air (123+011+001, with an unclear position of the eutectic point). The 123 phase melts at 1002°C incongruently similarly to that of 211 phase at about 1240°C. Our results [40] showed in O_2 atmosphere that the eutectic point lies at about 930°C (5mol% 100) followed by incongruent melting of the 123 phase at 999°C which is accompanied by the formation of the 142 phase later to decompose at about 1120°C. A very narrow region of only 123+liq cannot be excluded as also indicated in the phase diagram shown in Fig.1. While Laudise et al [36] reported the eutectic point below 900°C (<5mol% 100), Jishan et al [59] did not find this point at all. Aschage and Keefer [60] found incongruent melting of the 123 phase at 1015°C but did not report the existence of the other perovskite phase different from the ordinary 123 and 211 phases. In most reports mentioned above only the 132 compound was indicated instead of a more plausible composition of a "solid solution" around the 142 composition [40].

Both of the above pseudobinary diagrams are illustrated in Fig. 3 as based on the reported data [11,23,36] and our own experience [40] regardless of the differences due to the working atmospheres (air or flowing O_2). Some other cuts were reported, e.g., between CuO and $4BaO.YO_{1.5}$ [23], between the compositions 035 and 211 [58] and between 3BaO:CuO and the 123 phase [25] including the favoured composition used for the growth of 123 single crystals at the melt stoichiometry of about 1:4:10 or 4:30:66, respectively.

ANALOGOUS La-BASED AND Pt-SUBSTITUTED PHASES

It is clear that a deeper understanding of all the phases possibly occurring in the Y-Ba-Cu-O system requires further research. Some additional information should be taken into account as follows:

(i) In the comparable system of La-Ba-Cu-O [47] the following phases are reported: the 422, 212, 415 and 336. Both the systems in question (with Y or La) have at least one phase that is unique to it [47], e.g., the 211 compound and a solid solution from the 132 towards 021 (Y) and in contrast a solid solution around the 422 and 336 (with La).

(ii) Some of Pt enriched phases were reported to exist, for example:

1) $Y_2Ba_2Cu_3PtO_{10}$ [55],

2) $Y_2Ba_3(Cu_{1-x}Pt_x)_3O_9$ (x about 0.33) [48],

3) $ErBa_{1.03}Cu_{0.77}Pt_{0.46}O_{4.34}$ [49],

4) $YBa_2Cu_{3-x}Pt_xO_9$ (x about 0.33) [50],

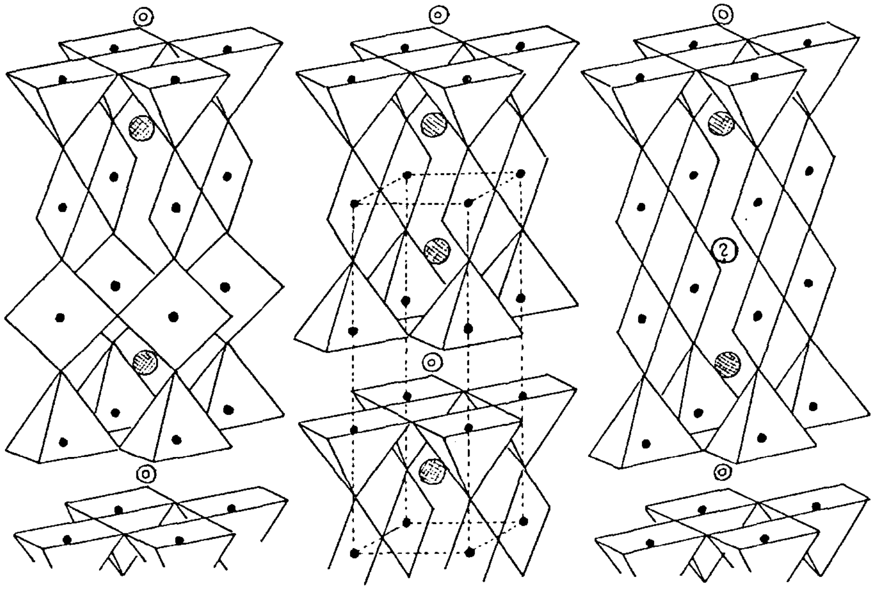
5) $Y_{20}Ba_{60}Cu_3Pt_{17}O_{77}$ [11],

(the second one to exist within the temperature region from 1050 to 1300 °C, the third one to possess an orthorhombic structure Pcmm, a= 10.287, b= 5.659 and c=13.157 Å). Formally assuming the Pt for Cu replacement the above phases can be read approximately as "224", "233", "445", "123", and "131". Except the 123, these phases were not found as pure (Pt-absent) compounds, (cf Table I).

The phase "131" found in our laboratory [11] seems to be similar to the single crystal of $Ba_4(Cu,Pt)O_6$ reported by Bykov et al [55] who also stressed that platinum in quantities less than 0.05 mol % were found in various single crystals of the rare-earth substituted 123, this contamination not hindering the superconductivity.

HYPOTHETICAL STOICHIOMETRY OF THE 123 DERIVED COMPOUNDS WITH MULTIPLIED COPPER OXIDE LAYERS

To predict new possible variants of the Y-Ba-Cu based compounds we have to look more closely at the structure of superconducting phases, e.g., the 123, cf Fig.4, middle. The oxygen deficient perovskite structure consists of layers of corner-sharing copper oxide octahedra (CuO_6) interlinked by corner-sharing square-planar CuO_4 units [56,57] which are probably responsible for superconductivity. Assuming that the increased number of these CuO_4 chains may result in the higher T_c [1] we can hypothetically analyse its importance regarding the stoichiometry change of the original 123 phase. Speculation on the known structural model of the 123 [1-5] shows that the multiplication of the CuO_4 chains (cf.Fig.4) would create between thus formed layers new crystallographic sites different from those corresponding to the standard



no extra site considered:	original 123 (CuO_4 layers multiplication:)	new site occupation: (?)=Ba	(?)=Y
1:2:4	twofold	1:3:4	1:1:2
1:2:5	threefold	1:4:5	3:2:5
1:2:6	fourfold	1:5:6	2:1:3

FIG.4.: Model of perovskite structure showing geometrical network of oxygen octahedral and tetrahedral units.The standard 123 compound is illustrated in the middle with the Cu-unit cell marked by dotted lines. Small solid, large shaded, doubled and containing question-mark circles represent Cu, Ba, Y and unknown cation.

ones occupied by yttrium and those occupied by barium in the coordinations made by eight and ten nearest oxygen atoms, respectively. The new sites would have the coordination eight and can be occupied by either yttrium or barium. Now we can choose whether to introduce yttrium to maintain its original coordination (eight) or to introduce barium to preserve the original periodicity (2Ba:1Y). The resulting stoichiometry of such phases would then be 112 and 134 for twofold and 325 and 145 for threefold multiplication of CuO_4 layers, respectively. (In addition the 1Y:1Ba mixed threefold phase would then exhibit a stoichiometry of 359). Evidently there is another chance how to multiply copper oxide chains, see Fig.4, left. The corner-sharing square-planar units can be joined perpendicularly and we can assume the newly created voids vaccant. The resulting stoichiometry is then 142 and 152 for twofold and threefold multiplication respectively.

DISCUSSION

I believe that the search for further new superconducting materials with still higher T_c will also bring newer ideas to our knowledge of crystalchemistry and technology of now already classical Y-Ba-Cu based phases. Recent studies have already disclosed the possible existence of some other phases responsible for certain anomalies ascribed to the presence of presumably metastable (?superconducting) phases. Among many others Oda et al [51] showed an irreversible steep decrease of electric resistivity for the composition 497 at -38°C and Erbil et al [52] found a dc-Josephson effect for the starting stoichiometry 171 at a temperature as high as +14°C (the composition being further analysed as consisting of the 661 and 231 areas). Char et al [62] reported the discovery of a superconducting phase 124 which exhibits strinking similarities between the normal state properties of this 248 (i.e. $Y_2Ba_4Cu_8O_{16-y}$) and the 2244 phase (i.e. $Ca_2Sr_4(Bi,Cu)_8O_{10+y}$) as a result of doubled CuO_4 and BiO_4 layers. Upon annealing this 124 phase at higher temperatures its T_c shifts from original 81K up to as high as 96K which is systematically several degrees higher than that obtained for the standard 123 phase.They speculated [62] that this higher T_c may result from strain factors or more likely from some sort of a new structural order generated by foults.

Non of the above predicted superconducting phases, however, were noticed in the above phase survey and it is questionable if they can exist in larger scale at all. The formation of different arrangements of the oxygen vacancies as well as the mutual ordering and possible multiplication of CuO_4 layers is very dependent on technological procedures applied during the material preparation. It is plausible that certain procedures may favour the creation of specific microphase relations and so the formation of such **defective structures** which become evidently unstable with respect to the original 123. We also cannot exclude a possible stabilizing effect of contaminations and/or substitutions so as to prolong the "stability" region of previously nonstable phases which, however, lies beyond the framework of this article . A deeper analyses of metastable and unstable phases (even during their short-life occurrence), byproducts [53], microstructure [58] etc. may be an aid for further progress in HTS.

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