

Phase diagrams in CuO_x based superconductors

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Abstract—The users oriented need for HTSC phase diagrams is discussed including the melt-textured growth, formation of glass-ceramics and conventional sintering affecting the weak links problems. CuO_x -based binaries (and associated stable/metastable compounds) are reviewed and jointly redrawn. The ternary system Y-Ba-Cu-(O) is surveyed including the effect of oxycarbonates and Pt-substitutes. The most important pseudobinary cuts are also presented. The role of oxygen pressure is shown for the disordering and superstructure formation of $\text{YBa}_2\text{Cu}_3\text{O}_x$ as well as for the reactions to form the other phases. The system Bi-Ca-Sr-Cu-(O) is analysed from the viewpoint of existing data and collectively illustrated. Glass crystallization and inherent formation of HTSC phases is also noticed. A completed list of relevant literature is enclosed.

INTRODUCTION

The pioneering discovery of high T superconductors (HTSC) resulted in enormous research work [1-13] on various sintered oxide samples aimed to the preparation of chemically and structurally single-phased ceramics. Although known for thousand of years, ceramic materials [1] are, in general, far from being fully understood due to the frequent overlapping of thermodynamic and kinetic phenomena and paradigm that properties depends on its structure which in turn depends on processing. Successful material treatment presupposes, however, a good knowledge of phase stable/metastable equilibria in the given system. The basic approach requires the classical search for phase diagrams and identification of compounds responsible for specific properties of HTSC. First interest was focused to $\text{La}_{2-x}(\text{Ba},\text{Sr})_x\text{CuO}_4$ (LSCO) latter extended to Y_2O_3 -BaO- CuO_x (YBCO) systems, typically $\text{YBa}_2\text{Cu}_3\text{O}_x$ (123). Phases with still higher T_c were found in the four component alkaline earth bismuth or thallium cuprates belonging mostly to a homologous series $(\text{Bi},\text{Tl})_2(\text{Sr},\text{Ba})\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ (BCSCO) although another series $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{3+2n}$ can also lead to HTSC. Still another HTSC compounds have been discovered, such as $(\text{RE},\text{Y})_{1+x}(\text{Ba},\text{Sr})_{2-x}\text{Cu}_3\text{O}_{6+y}$ (where RE = rare earth) $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+y}$, $\text{Pb}_2\text{SrLaCu}_2\text{O}_{6+y}$, $\text{Ba}_{1-x}\text{K}_x\text{Bi}(\text{Pb})\text{O}_{3+y}$ or $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, and proposed [13]. Although the Tl-based HTSC show the largest values of T_c about 125 K, the relevant phases and particularly their equilibria have not been determined yet owing to the extreme volatility of Tl compounds as well as the poisonous nature of their vapours.

In order to understand the equilibria and possible metastable phase formation of the various HTSC phases it is necessary to know the reactions of all the boundary systems. Because HTSC are complex oxides of the perovskite family the specialised studies are required to find necessary relations between processing parameters, oxygen concentration and its spacial distribution, defect characteristics and optimum superconducting properties. Most of our current knowledge, however, is confined to reactions in air having little data for any but the HTSC phases themselves in variable p_{O_2} and even less information for CO_2 contaminated atmospheres. The users oriented needs for these phase diagrams can be as follows:

- (i) Growth of single crystals upon slow cooling of nonstoichiometric melts where grown crystals are separated from parent matrix,

- (ii) Growth of crystallites from glassy solids prepared by melt rapid cooling where the mixture of crystalline and noncrystalline phases (glass-ceramics) is directly used without further separation,
- (j) Conventional preparation of sintered ceramics by standard heat treatments from various precursors and
- (jj) Deposition of thin films aimed to an understanding of the second phase formation and thermodynamic stability at low pressures.

To become even more complicated, several methods were investigated as to improve the intergranular contact by e.g. adding the modification oxides of Ag_2O , SnO or PbO or even elements such as Gd or Ag in attempt to remove the parasitic secondary phases enhancing often undesirable grain growth. Additives were inserted mechanically or even segregated during the precipitation processes (e.g. during glass crystallization). While the exact nature of the weak-link problems in the sintered HTSC is still under intense investigation, it has recently been demonstrated that the problem can be greatly reduced by a new method of melt-textured growth [14-15] consisting of the directional spherulitic solidification used instead of the conventional melt-free sintering (where, on contrary, the presence of melted regions, often rich of copper oxides, was considered undesirable as reducing good superconducting properties due to the formation of closed-porous morphology). Melt-textured samples, however, are not a single phase because the 123 starting material transforms to a mixture of 211 (=2Y:1Ba:1Cu) and yttrium-deficient liquid when it is heated in air above its incongruent melting of about 1010°C . The 123 reforms at the 211-liquid interface when the material is cooled below the melting point, thereby encasing the 211 crystals in 123. As is typical in any peritectic reaction a complete reaction between the high-temperature 211 solid and liquid is inhibited by the low-temperature 123 solid. This fractional crystallization embeds some 211 crystals in the 123 matrix and segregates the yttria-deficient liquid to the 123 grain boundary. It was reasoned, however, that producing a fine, homogeneous distribution of 211 in the liquid would minimize the amount of fractional crystallization and thus increase the connectivity between 123 grains. In turn, because 211 is formed by a peritectic reaction between Y_2O_3 and liquid, it can be distributed more evenly in the melt only if Y_2O_3 was distributed evenly in the melt first by short melting of 123 at about 1400°C .

Unlike metal forming processes the full-melting route [18] of ceramics preparation is not generally used since the refractory-like oxides have large volume changes during the solidification and in combination with the brittle nature of ceramics in the solid-state it causes cracking during the solidification process. On the other hand the melt-processing technique has been investigated with several ideas well known from the metal production of metallic glasses [1,16,17] and has an advantage of fine microstructures, reduced segregation, extended solid solubility, and last but not least, the formation of new types of phases. So it is assumed that the full-melting process allows one to fabricate materials with oriented microstructures and with tailorable solid-state properties [18-20]. However, nonequilibrium (real) conditions of the solidification [21-24], often faced during rapid cooling [21], requires a more extensive knowledge of the location of phase boundaries usually to be extrapolated to the metastable regions or shifted to the unstable neighbourhoods [22-24]. The extrapolation is necessary for the description of the retarded nucleation whereas the shift is requested to characterize the slow transport phenomena. These are linked in the recently developed field of kinetic phase diagrams [22] including the customary T-T-T and less conventional C-T diagrams [1,21-23]. During the application of all experimental methods it is important to bear in mind in what manner the material is studied, whether at the actual (working) temperature or in the quenched (frozen) state. For the latter methods one must be sure that the preservation of the high-temperature state is guaranteed. For the elimination of secondary phase crystallized upon the melt solidification as well as the contamination by corroded crucible material a simple "soaking" method can be used [25].

As shown herewith a review of the literature together with experimental data is mostly used to construct plausible phase diagrams [23,24]. As

the amount of information quickly grew beyond the ability of any individual to absorb all the published data, the types of information available and the user aspects of the studies became more specialised. Besides the engineering applications, where the needs for phase equilibria are mostly directed to the field of synthesis of single phased ceramics or single crystals, specialised studies are required for the optimization of high J_c , apparently related to the formation of "pinning-sites" which may be due to the emplacement of impurity atoms or microdomains of a secondary phase. Oxycarbonated YBCO compounds are often easy to form likely to precipitate on the concave porous while the enrichment of copper may take place along the convex grain surfaces of a very small diameter. The Cu-rich phase boundary can easier vitrify to form an insulation envelope to pose a perpetual problem to achieving high current densities. However, the same grain boundaries could prove beneficial in preventing an attack by the atmosphere (e.g. $\text{CO}_2, \text{H}_2\text{O}$). Such grain boundaries of a different composition could also act as flux pinning sites. If the state, composition and particularly thickness of the grain boundaries is controlled in such a manner that it does not interfere with the percolation length it again could prove to be beneficial.

YBCO PHASES AND PHASE DIAGRAMS

The starting information is conveniently provided by the binary phase diagrams recently survived in [26-32] as based on the original studies [33-44]. The phase diagram of the Cu-O system was proposed less recently [33,34] using thermal, dissociation and microscopic data of a number of previous authors. CuO and Cu_2O were indicated as phases of a fixed composition with negligible departures from stoichiometry. These oxide form eutectics at about 68mol% Cu_2O and melt at 1075°C . Under oxygen pressure of 1atm, melting of heated CuO occurs at about 1110°C and is accompanied by the loss of oxygen and formation of an oxygen-deficient liquid phase (slag). With a further temperature increase the loss of oxygen becomes more progressive and at about 1400°C a saturated solution of oxygen in liquid copper is formed. In air, Cu_2O is formed at about 1020°C , followed by melting at about 1120°C to produce the liquid metal. When studying these phase stabilities in metal oxides it is important to ascertain them as a function of both temperature and oxygen pressure. If considering the above simple binary Cu-O system and if oxygen is titrated into a closed chamber containing the pure copper at a constant temperature, then the oxygen will be absorbed by the metal until the chemical potentials of both oxygens in the copper and surrounding gas are the same. If still more oxygen is inserted, then the metal will continue to oxidise, a metal oxide Cu_2O will begin to form and two-phase mixture of oxygen-saturated metal $\text{Cu}(\text{O}_2)$ and Cu_2O will be present. It can be shown schematically by the lines in activity-temperature phase diagram, see Fig. 1a. This is important for all the YBCO compounds based on CuO , so that the role of oxygen as free component must be taken in mind to distinguish between the conveniently closed Y-Ba-Cu-O and partly open Y-Ba-Cu-(O) systems. In addition to the classical description one more equation is valid in the latter case; this expresses the equality between the oxygen chemical potentials of the surrounding atmosphere (which is the subject of control) and that of the condensed phases in question. As a consequence, the number of degrees of freedom is reduced by one so that the usual form of phase ruling applies as if the system consisted only of the fixed non-volatile components. The concentration of fixed components must then be presented in quantities which are independent of the actual content of the free component (oxygen). Following this concept and accounting for the knowledge of double-oxide phases the expected phase relations in the $\text{Me}_1\text{-Me}_2\text{-O}$ system can be suggested in the form of quasibinary x-T diagrams [32], see e.g. Fig. 1a. It is worth noting that with increasing temperature the stability of oxygen-poor solid phases can increase while that of oxygen-rich melts decreases; this may result in solidification on heating and in melting upon cooling of the samples of given composition. Owing to the existance of two or three partly immiscible melts, more than one liquidus curve can be observed which may disrupt the conventional procedures of phase equilibria investigation.

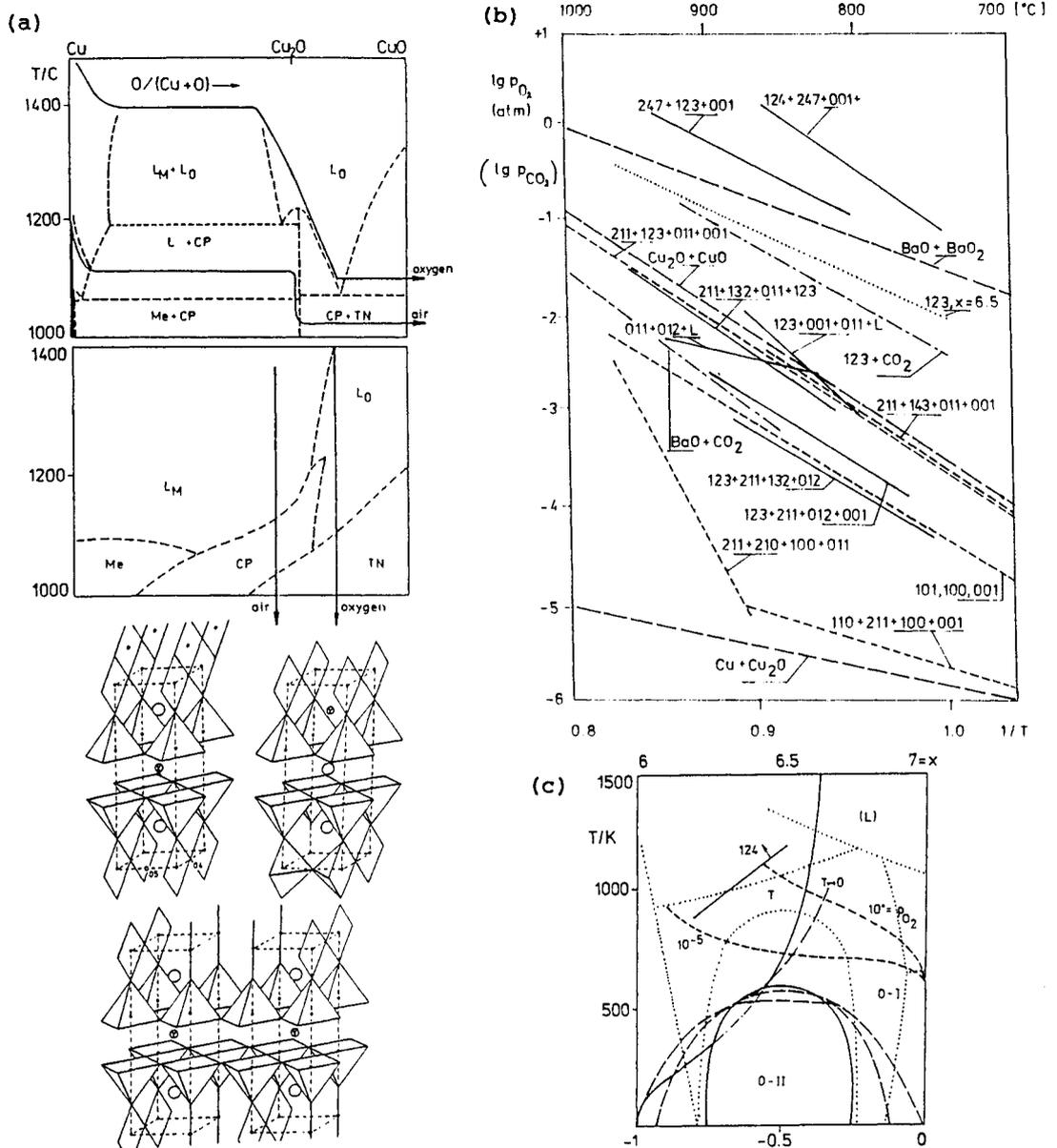


Fig. 1: Effect of oxygen on phase formation in the CuO-based YBCO. (a) Phase relations and activity plots in the Cu-O system^x [32]. (b) The pseudobinary phase diagram 123-0 originally proposed by Hauck et al [63] (dotted) on basis of TG measurements completed by lines calculated by Khachatryan et al [64] (dashed) and added by data of Bayers and Ahn [71] (solid). The upper solid line represent the limit of 124 existence while the upper dashed lines are isobaric curves transferred from Lindemer et al [66]. The spherical models of the perovskite unit cell of the 123 compound in question are also included with the Cu sites marked by small solid circles to illustrate oxygen reordering: upper left showing plausible formation of 237 or 124 compounds by inserting one extra CuO-layer to every second or every 123 unit cell (marked by dashed lines), upper right illustrating possible cation (Y instead Ba, e⁻→O) and anion (O₄→O₅) disordering and lower part showing the gradual formation of superstructures likely accompanying the change of oxygen content from tetragonal (X=6) to orthorhombic (X=7) structures, oxygen being inserted to occupy O(4) sites to form CuO sheets along b-axis one every third, two every fifth or one every second 123 unit cell [61]. (c) Temperature dependence of oxygen pressure for the various reactions marked as compiled from Bayers and Ahn [71] (dotted), Lindemer et al [66] (solid), Borowiec et al [74] (dashed) and Fjellvag et al [72] (dash-and-dotted).

Let us discuss some of CuO containing binaries and associated compounds. In the BaO-CuO system^x the barium cuprate 011 was described to exist in air [35,40] and to melt incongruently between $1010-1020^\circ\text{C}$. It seems to have a wide P_{O_2} stability range possessing the actual chemical formula BaCuO_{2-y} where the exact cations ratio is still in doubt but is known to react quickly with moisture. The compound 012 is more acknowledged [40,41,47] and is anticipated that its actual formula is again $\text{BaCu}_2\text{O}_{2-y}$, but its P_{O_2} stability limits are not known. The compound $\text{Ba-Cu}_2\text{O}_5$ is known to occur at low P_{O_2} and is an important impurity phase found in processing of the 123, especially below 1 atm. It is also known, however, that this phase is formed in air from specimens which have partially melted during processing. Apparently the ternary eutectic liquid formed in air (with $<3\% \text{Y}_2\text{O}_3$) can lose enough oxygen so that a $\text{BaCu}_2\text{O}_{2-y}$ phase can metastably crystallize from the melt where the amount of oxidation is dependent on the cooling rate. In $\text{P}_{\text{O}_2}=1$ atm the compound of 021 is formed but its exact stability limits have not been investigated. It is again very sensitive to atmospheric moisture. The compound 023 is apparently quite stable but is known to quickly decompose to BaCO_3 when heated in the presence of CO_2 having the true decomposition temperature about 800°C for all oxygen pressures. The phase 035 was also discussed [47,26-29,58] to exist as a single compounds but not confirmed yet. In spite of many published phase diagrams the binary system $\text{BaO-Y}_2\text{O}_3$ contains probably only two compounds, Y_2BaO_4 (210, decomposing peritectically at about 1030°C to the 430) and $\text{Y}_4\text{Ba}_3\text{O}_9$ (430, melting incongruently at 2160°C); all other phases 110, 210 and 340 being plausibly oxycarbonates [73] such as $\text{Y}_2\text{Ba}_4\text{O}_7\cdot\text{CO}_2$ (with a determined tetragonal unit cell). All these "other" phases cannot be probably synthesized in atmospheres containing less than 5 ppm CO_2 which otherwise poses a high demand to the gases purification. In the $\text{Y}_2\text{O}_3\text{-CuO}$ system the major orthorhombic compound is the yttrium cuprate 101 [36] to melt incongruently between $1150-1180^\circ\text{C}$ with the eutectic temperatures about 1075°C (for 7.5mol% Y_2O_3) [39]. This is the only system that does not seem to be affected by CO_2 , although, it is quite sensitive to P_{O_2} . The compound $\text{Y}_2\text{Cu}_2\text{O}_5$ can be reduced to YCuO_2 by heating in argon or nitrogen at 1000°C . The latter phase exhibits the dellafossite structure and shows poly-typic stacking faults which are probably very sensitive to impurities in the gas and can be easily oxidised by heating in O_2 at about 500°C to $\text{Y}_2\text{Cu}_2\text{O}_5$ being again very sensitive to the actual P_{O_2} .

The ternary system $\text{Y}_2\text{O}_3\text{-BaO-CuO}$ has probably been the most heavily investigated system in the shortest^x period of time of the recorded history of oxide equilibria studies, so the the detailed survey is almost impossible, see for example, reviews [26-32]. The first reports on these diagrams were all done in air [27,42,47,58] and bears a basic agreements on location of the most important tectic points. The further areas of agreement are with respect to the existence of the two ternary phases 123 and 211 and associated pseudobinary joins. In addition, in the early literature there were reported further ternary compounds such as 213, 132, 143, 142, 385, 152, 235 or 131 sometime proposed in accordance with the comparable system of La-Ba-Cu-O (phases 422, 212, 415 and 336). However, the major culprit responsible for the conflicting data in the BaO -rich portion of the system is a phase generally referred to as "the other perovskite" variously labeled as 132, 142, 143, 385 or even 184. It is generally agreed that this phase may have a variable cation ratio and that it can be oxidized and reduced during the heat treatment. Although early assumed to exist only as an oxycarbonate there is not a definite agreement whether or not it must contain CO_2 in order to exist as a stable phase. The situation is further complicated by the existence of noble metal (often Pt) enriched phases such as 224 = $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{PtO}_{10}$, 233 = $\text{Y}_2\text{Ba}_3(\text{Cu}_{1-x}\text{Pt}_x)_3\text{O}_9$ for $x < 0.33$, "123" = $\text{YBa}_2\text{Cu}_3\text{-xPt}_x\text{O}_9$ for $x < 0.33$ or 131 = $\text{Y}_{20}\text{Ba}_{60}\text{Cu}_3\text{Pt}_{17}\text{O}_{77}$. The equilibrium phase relations at a constant and predetermined P_{O_2} can be represented by a triangle with the fixed components at the corners only if the barycentric coordinates are chosen to be independent of the real oxygen content. From the point of view of single crystal growth the most interesting diagrams were reported in [28,30,49] who assembled the area along the four directions starting

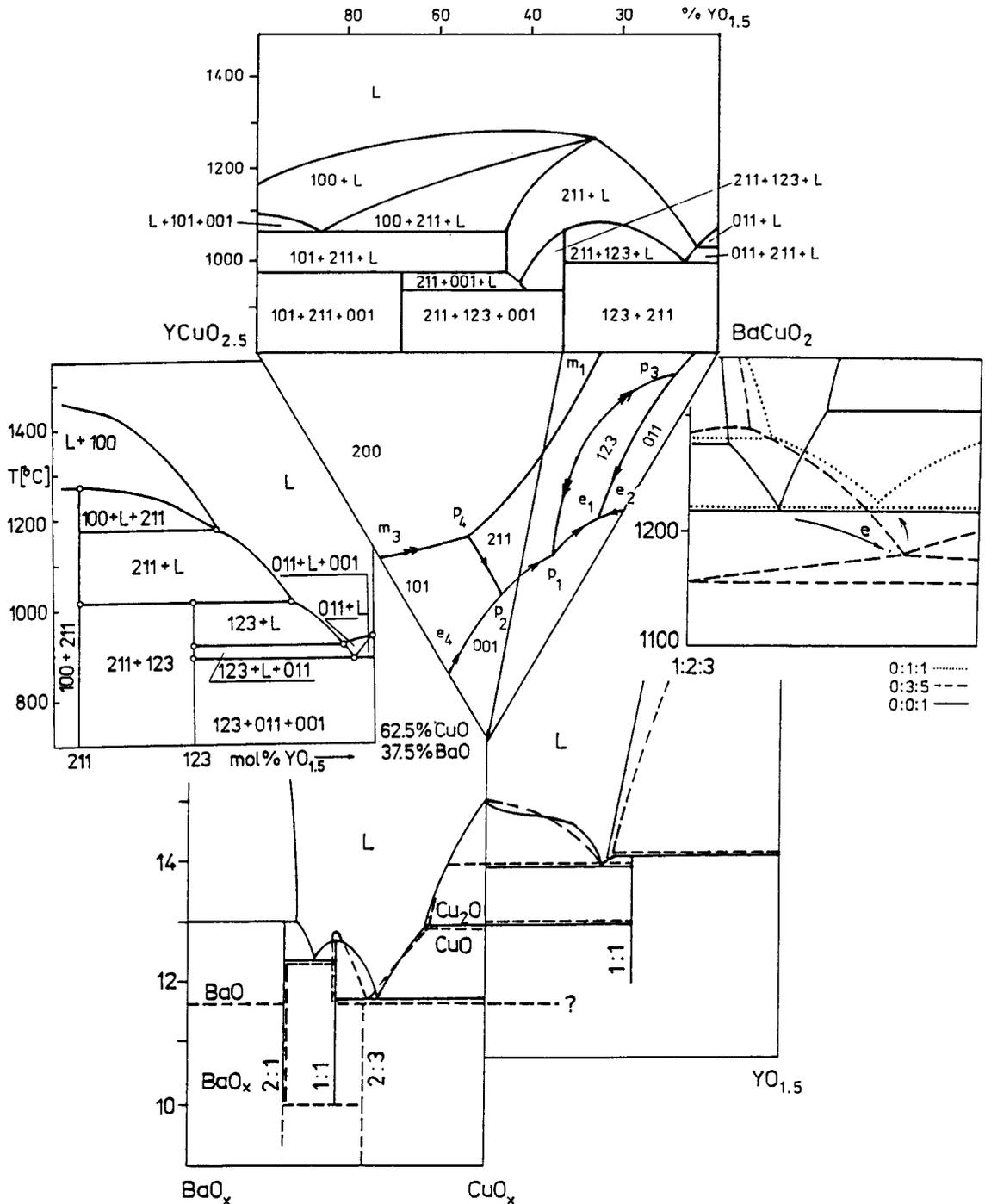


Fig. 2: Experimentally determined and literature corrected pseudobinary cut $\text{YCu}_{2.5}\text{-BaCuO}_2$ in oxygen [27-32] completed with the CuO_x -rich ternary corner showing the slightly modified liquidus surfaces [51] in the middle triangle. The numbers represent the ratios Y:Ba:Cu and the letters m, e and p characteristic temperatures of melting, eutectic and peritectic points to reach approximately $P_1=940$, $P_2=975$, $P_3=1000$, $e_1=890$, $e_2=920$, $e_4=1110$ and $m_3=1120^\circ\text{C}$. Left is the convenient pseudobinary cut derived from [27-32,55] and in the right there are three superposed pseudobinary cuts computer calculated in [52,55]. Lower two binary diagrams [30] show experimental (dashed) [40] and calculated [55] lines.

from the 123 phase towards CuO , $\text{Ba}_3\text{Cu}_{12}\text{O}_{15}$, $\text{Ba}_3\text{Cu}_7\text{O}_{10}$ and $\text{Ba}_3\text{Cu}_5\text{O}_8$, latter approved by theoretical calculations in [55]. The phase relations in the system 001-011-123 at 950°C in O_2 were shown in [25,28]. Phase relations in the CuO -rich corner of the $\text{Y}_{0.5}\text{-BaO-CuO}$ ternary was determined in [50] and is included in the middle triangle of Fig.2 showing in addition one of the most intensively investigated tie-line between 101 and 011 [26-32,44-54]. There were identified eleven invariant reactions involving liquids and their corresponding invariant temperatures which explains the drastic changes in the microstructure of sintered ceramic samples that are produced by a small deviations from the 1:2:3 stoichiometry. Samples containing CuO as a second phase are typically denser and have larger grains than stoichiometric or Cu -deficient samples prepared in the same manner at 950°C . A pseudoperitectic reaction at 940°C explains this behaviour as the liquid phase promotes densification and grain growth. However, the resolidification results in nonsuperconducting phases in the grain boundaries between 123 crystals as discussed for directional solidification in the introduction. Another very important cut is that between 123 and 211 [26-32] which is shown in Fig. 2.

The only computer calculation of phase diagrams for the $\text{Y}_{0.5}\text{-BaO-CuO}$ system was presented in [55]. It was based on a two-sublattice⁵ regular solution model for ionic solution of the 123. The calculated boundary lines were in fair agreement with the experimental data reported by several authors. The calculated vertical section containing 211 and 123 plotted against the edge 011-001 indicated that decreasing P_{O_2} decreases melting temperatures [57] of 123 and increases the liquidus composition range of liquidus/123 two-phase equilibrium. Assuming that the liquidus temperature decrease with P_{O_2} the change of liquidus surface with oxygen pressure may provide new routes for isothermal single crystal growth. Further studies of the YBCO system in high oxygen pressures have yielded valuable insight into the formation of two additional HTSC, i.e., 247 ($\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{13+y}$) and 124 [59-62] where the 124 structure is made by inserting an extra-Cu-O layer between the Ba-O layers in every 123 unit cell while 247 in every other 123 unit cell. This structure was initially observed as an isolated defect in bulk 123 samples and ordered defects in the post-annealed films. With understanding gained from oxygen high-pressure studies [62] the controlled decomposition of 124 into 123 and CuO was realised to become a tool for a practical technique of flux pinning enhancement in 123 because the most of the CuO precipitates as extremely thin platelets within the 123 grains. Unfortunately, the intergranular critical currents densities remain still poor because the randomly oriented fine-grained microstructure of the 124 precursor is retained in the 123 that forms. Nevertheless the existence of 247 and 124 implies that there must be an additional invariant reaction and corresponding changes in the phase relations near the 123 associated with the increasing P_{O_2} . The potential use of hot isostatic pressing to increase the density of the 123 motivated several studies to seek the decomposition of pure 123 to 247 or 124 in high P_{O_2} which resulted, however, in breakdown of the 123 into 211 and 035 or to a more definite 023.

As can be seen from the pseudobinary phase diagram [63,64] in Fig.1b the precise stoichiometry of 123 is sensitive to a careful control of the temperature, oxygen pressure and cooling rate and exhibit some superstructures (Ortho II) between the fully-oxygenated 123 (Ortho I) and deoxygenated Tetra. In contradiction to a common believe that the standard T_c plateaus (on the plot T_c vs X) correspond to single-phase regions of 60°C and 90°K HTSC we can associate it with superlattices [61] for $X=6.61$ $\{\frac{1}{3}00\}$, 6.65 $\{\frac{2}{5}00\}$ and $X=6.85$ $\{\frac{1}{2}00\}$ and progression of ordered structures but not a mixture of crystals. In their view we have to question whether it is best to think of the 123 as a nonstoichiometric phase or as a series of ordered phases with only a small differences in oxygen content. These fine structures are certainly difficult to prepare as a well-ordered bulk phase because oxygen diffusion [78-80] is considerably reduced at the temperatures where the structures became stable. It is worth noting that when oxygen content approaches $X=7$ the 123 lost its granular signature as the flux pinning declined due to absence of oxygen-deficient regions (probably empty chains in the 123 structure)

acting as desired pinning centers. Not less clear are the reactions taking place within the complex Y-Ba-Cu-O system. A number of invariant reactions have an important application for processing the 123 in reduced oxygen pressures. $\text{BaCu}_2\text{O}_{2-y}$ is stable over a wide range of reduced P_{O_2} so it is one of the keys to better understanding of quaternary phase relations because its participation in several important reactions including the 123 decomposition. Although "132" is not stable in contact with the 123 in air it becomes stable at low P_{O_2} and it may even act as a nucleation site for the a-axis oriented 123. The review of previous synthesis studied is aided by Fig.1c [65-74], as investigated with respect of phase stability by the conventional van't Hoff plot of $\log p_{\text{O}_2}$ vs $1/T$. It relates to the oxygen potential plot sometime called Ellingham diagram which best illustrates the complex relationships in the system when the oxygen potential controls the oxidation state of several of the metals involved [70,71]. Beside known Cu-, Ba-, BaCO_3 - and $-\text{O}_2$ relations it is important [68] to study the reactivity 123-001-211-"132"-012- O_2 [69]. Not less important is the 123 reaction with CO_2 with a partial pressure of CO_2 in O_2 [72]. EMF values were reported in order to determine mutual stability of phase under question [74] following the order 123, 143, 385 and 152. From the measured oxygen potential the Gibbs energies were calculated and positive reactions entropies were analysed in terms of the plausible metastability of phases. It is readily apparent from the Fig.1c that the data are yet inconsistent and requires still more detailed studies and thermodynamic basis like in [75].

PHASES AND PHASE DIAGRAMS IN THE BCSCO SYSTEM

For the system Bi-Ca-Sr-Cu-(O) the situation is even more complicated due to the presence of an additional fifth cation [30]. Moreover, the disorder and off-stoichiometry on the cation sites can occur to a greater extent than in YBCO. Known binary edges [81-89] are collectively shown in Fig.3 [90-95] and completed by only known pseudobinary cut [93]. The system Bi_2O_3 -SrO [82] and Bi_2O_3 -CaO [81] were previously reported. Phases SrBi_2O_4 , $\text{Ca}_4\text{Bi}_6\text{O}_{13}$, $\text{Ca}_2\text{Bi}_2\text{O}_5$ and $\text{Sr}_2\text{Bi}_2\text{O}_5$ are known the latter transforming to $\text{Sr}_{0.9}\text{Bi}_{1.1}\text{O}_{2.55}$ melting incongruently at 985°C . $\text{Sr}_3\text{Bi}_2\text{O}_6$ is the most stable phase melting incongruently to SrO plus liquid at about 1210°C and $\text{Sr}_6\text{Bi}_2\text{O}_9$ decomposes in the solid state at about 965°C to $\text{Sr}_3\text{Bi}_2\text{O}_6$. The rhombohedral Sillen-phase shows solid solution $\text{Sr}_{0.5}\text{Bi}_{1.5}\text{O}_{2.75}$ with its maximum at the melting curve at 960°C and 840°C (with CaO). There are supposed to exist some superstructures due to the oxygen-vacancy ordering near to the minimum eutectoid and maximum CaO, further two phases of the approximate ratios of 5:14 and 1:2 may occur due to Ca/Bi ordering. CaBi_2O_4 transforms at about 725°C to the solid solution plus $\text{Ca}_4\text{Bi}_6\text{O}_{13}$ which again transforms and shows superstructure. $\text{Ca}_2\text{Bi}_2\text{O}_5$ transforms to an unknown polymorph at about 885 - 925°C (at low and high CaO sides). Bi_2O_3 - CuO_x phase diagram was published in [84] apparently containing only one compound Bi_2CuO_4 showing that its melting relations have a little effect on the phase relations of the quaternary system in question. SrO-CuO_x [85] and CaO-CuO_x [87] were reported. Sr_2CuO_3 melts incongruently at about 1085°C as well as the other compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (955°C). From a practical point of view the actual melting are essentially effected by reactions with container material such as Pt, Au, Al_2O_3 etc. Ca_2CuO_3 and CaCu_2O_3 exist to 1030 and 1018°C respectively and $\text{Ca}_{45.3}\text{Cu}_{54.7}\text{O}_2$ ($P_{\text{O}_2}=1$ atm) stoichiometry varies with P_{O_2} and synthesis conditions. The ternary system SrO-CaO-CuO [86,87] exhibits three solid-solution series which extend from the SrO-CuO edge towards that of CaO-CuO, Ca^{2+} substituting for Sr^{2+} so Sr_2CuO_3 and Ca_2CuO_3 being essentially isostructural. The 14:24 ratio of solid-solution extends from the compound $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ to about (Ca_7Sr_7) showing a ternary phase with a very limited homogeneity region of $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ (Ba,Sr) $_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ in which all the Tl and Bi layers have been removed leaving only Cu-O layers alternating with that of (Sr,Ca)-O. Note that although SrO can substitute for CaO in several of the phases there

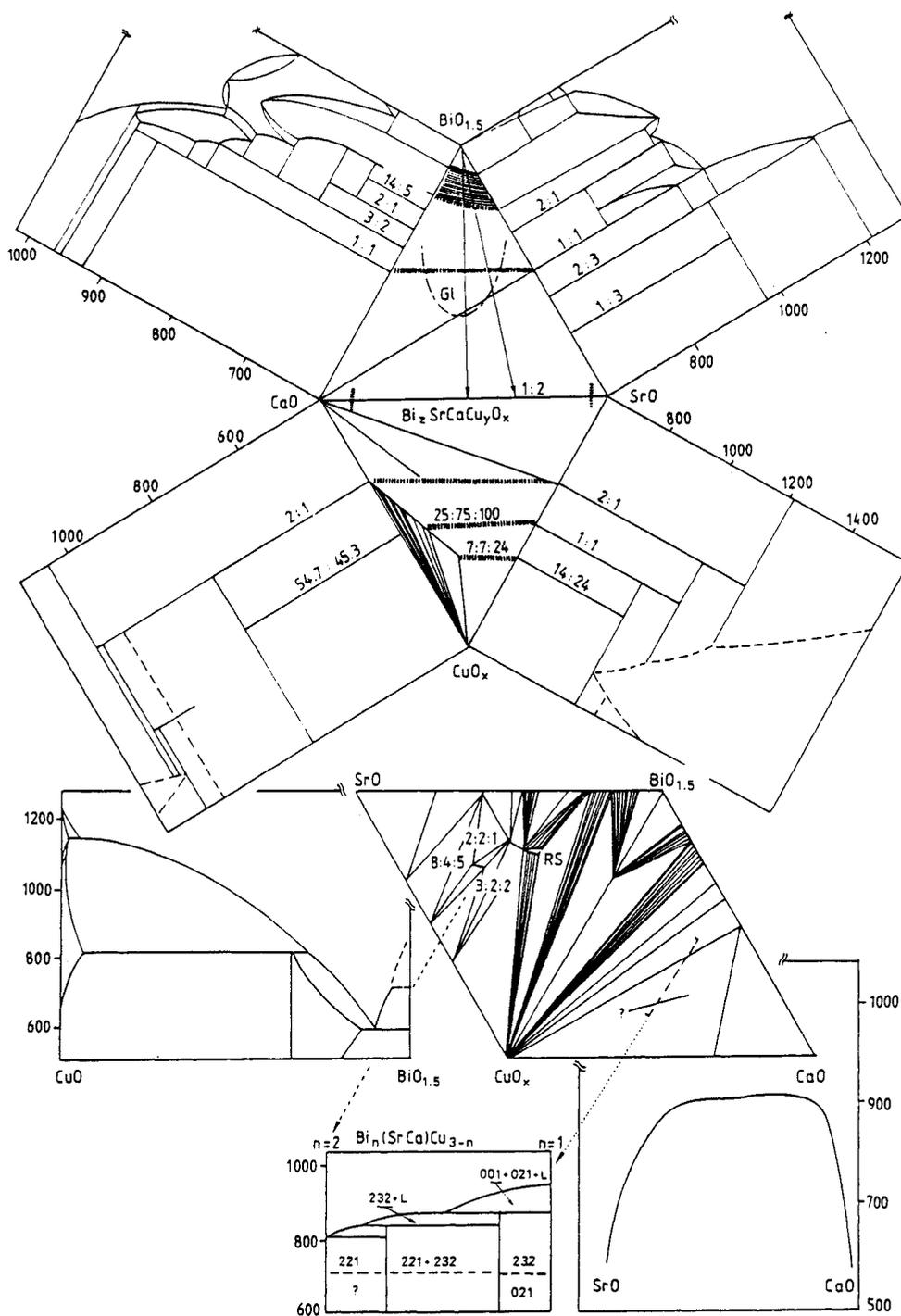


Fig. 3: Complex view to BCSCO system, the upper part showing the binary edges of CaO-CuO , SrO-CuO , $\text{CaO-BiO}_{1.5}$ and $\text{SrO-BiO}_{1.5}$ [80-88] including the associated pseudoternary triangles with the marked solid solution, isostructural joins (dotted), glass-forming regions (dash-and-dotted) and ternary phases (numbers representing the ratios $\text{Bi}:\text{Ca}:\text{Sr}:\text{Cu}$). The lower part illustrates the two remaining binaries and ternaries [30,90-101] completed by only known pseudobinary cut [94]. The lines presented are valid for subsolidus regions at approximately 900°C and R_{SS} abbreviates Raveau-type solid solution.

is no evidence of the opposite substitution. Complementary compound was found with Ba instead Sr as $Ba_4CaCu_3O_x$ [96] and solid solution with Pb instead Cu as $Sr_xCa_{1-x}PbO_4$ [94,95] but not including binary $SrPbO_3$.

There are four ternary phases [30,90] $Sr_{1-8-x}Bi_{2.2+x}Cu_{1-x/2}O_y$, solid solution labeled the Raveau-phase with a corresponding general formula $Sr_{1-8-x}Bi_{2.2+x}Cu_{1-x/2}O_y$, $Sr_3Bi_2Cu_2O_8$ and $Sr_2Bi_2CuO_6$ which should nominally be the phase with $n=1$ [88] having no Ca-O layers. Instead it, however, a different phase is formed exhibiting a gross deficiency in SrO content [30,88] (about $Sr_{16}Bi_{17}Cu_7O_x$). It was indicated that the $Sr_3Bi_2Cu_2O_8$ is a unique phase, however, no single crystals have been synthesized probably existing also in the form $Bi_{2+x}(Ca,Sr)_{3-y}Cu_2O_8$. Single phase specimens of $Bi_4Sr_8Cu_5O_{19+x}$ were obtained [90] when the starting material were annealed in oxygen atmosphere. Superconductivity apparently occurs at the higher SrO contents and likely for some metastable compositions of R_{ss} ($x < 0$). Single layered $Sr_2Bi_2CuO_6$ has actually more Bi and less Sr. The only pseudobinary cut was reported on the line $1 < n < 2$ of the system $Bi_n(SrCa)Cu_{3-n}O_x$ [93] locating the HTS phase 2(3)2 (i.e. $Bi_2(Sr,Ca)_3Cu_2O_x$) and the semiconductor phase 2(2)1. The liquidus line of the HTS phase was found to lie in the region $1.6 < n < 1.875$ enabling possibly the single crystal growth. It was conjectured that the glassy phase first formed from the quenched melt undergoes crystallization of the 2(2)1 phase below $700^\circ C$. There are some miscellaneous phases of not yet approved composition such as Bi:Sr:Cu ratios as 2:4:1 and 1:2:1 as well as 4:9:1 and 2:7:2 the latter two being synthesized at the presence of a mineralizer Li_2CO_3 [89]. It was noticed that while a phase does exist at the ideal 2:2:1 ratio it is not superconducting, instead, superconductivity occurs in a nearby Sr-deficient phase. There are more detailed studies showing the phase relations in the associated four-component system [30,89-101] final resolution still missing. General agreement seems to exist that the two-layer phase 2122 can be synthesized essentially single phased at the 3334 composition but not at the starting required stoichiometry 2122. It is agreeable that the three-layer phase 2223 is more stable with addition of PbO [94] but there is little evidence to be a true single phase in the pure quaternary system. It is plausible that 2122 phase forms a pseudobinary joins with CaO , $(Sr,Ca)_2CuO_3$, $(Sr,Ca)_{14}Cu_{24}O_{41}$, CuO , $Sr_6Bi_2O_9$, L and R_{ss} .

Further interesting area is the low temperature crystallization of rapidly solidified melts [18-20,102-107] which first yields nonsuperconductive phase(s) latter rereacting with the remaining glassy matrix to form first the low T_c and then the high T_c phases. The heat treated 1112 (including its partly Pb-substitutes) showed a low temperature crystallization ($600^\circ C$) of $(Sr,Ca)_3Cu_5O_x$ (together with some impurity phases such as Ca_2PbO_4) which latter react to form the low T_c phase. The 2425 rapidly solidified composition [104] showed the evolution of the high T_c phase out from the 2122 phase which in turn is developed from the 2021 phase (exhibiting as low T_c as 12 K). The high T_c phase is formed at $865^\circ C$ in the presence of a liquid phase rich of copper and calcium as verified by the presence of CuO and $(Ca,Sr)_2CuO_3$ phases at the solid-liquid interface. The investigation of the Pb-doped Bi-based glasses confirmed that the first phase to precipitate around $500^\circ C$ is $Bi_{2+x}(Ca,Sr)_{2-x}CuO_{4-y}$ to produce on further annealing the low T_c phase around $800^\circ C$. It was noticed, however, that the 2212 crystals grow relatively fast leaving behind a Cu- and Ca-rich regions resulting in the inhomogeneity of originally fine glass matrix [97,104-107]. The high T_c phase will form at the interfaces after certain amounts of Ca and Cu have diffused in the low T_c phase adding so one more Ca-O and Cu-O planes.

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