Phase compatibilities of $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ type structure in quintenary systems $\text{Y}--\text{Ba}--\text{Cu}--\text{O}--\text{X}$ (impurity)

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Electrical transport properties of the oxidic high $T_c$ superconductors are significantly affected by the presence of minor amounts of various elements adventing as impurities, e.g., from the chemical environment during manufacturing. $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ is prone to an extinction of the superconductivity on (partial) substitution of all four elemental components. E.g., $\text{Pr}$ (for $\text{Y}$), $\text{La}$ (for $\text{Ba}$), $\text{Zn}$ (for $\text{Cu}$) or peroxygroup (for $\text{O}$) substituents will alter some of the superconductivity preconditions, like mixed valence state in $[\text{Cu}_3\text{O}_{1-\delta}$] network or structural distortion of the network. Although various pseudoternary chemical equilibrium phase diagrams of the $\text{Y(O)}--\text{Ba(O)}--\text{Cu(O)}$ system now are available, no consensus is generally shown, however, this is partly due to lack of compatible definitions of the equilibrium conditions. Less information is available about the phase compatibilities in the appropriate quaternary phase diagram (including oxygen) and virtually no information exists about any pentenary phase diagrams (including one impurity). Unfortunately, complexity of such systems, stemming both from number of (yet mostly uncharacterized and unknown) quaternary or pentenary compounds and from visualizing the five-component phase system, limits this presentation to more or less close surroundings of the $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ type phase in appropriate pseudoquaternary or pseudopseudoternary diagrams, involving $\text{Y}--\text{Ba}--\text{Cu}$ and $\text{O}, \text{O}_2\text{CO}_2$, alkaline metals, $\text{Mg}$ and alkaline earths, and $\text{Sc}$ and most of the $3\text{-d}$ and $4\text{-f}$ elements. The systems were investigated by means of $X$-ray diffraction, neutron diffraction and chemical analytical methods on samples prepared by sol–gel technique from citrates. The superconductivity was characterized by measuring the diamagnetic susceptibility by SQUID.

Substitution for oxygen. One of the most characteristic features of $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ is the reversible oxygen uptake, driven by the gas partial pressure. Formally, it can be considered as substitution of oxygen by vacancies. At high oxygen partial pressures (well above 1 atm) the structure is in principle preserved, but some of the O-site apparently accommodate peroxy groups (their presence in samples prepared even at ambient oxygen pressures is assumed). Low oxygen partial pressures will on the other hand lead to decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{5.91}$ into $\text{Cu}_2\text{O}, \text{Y}_2\text{BaCuO}_5$ and probably $\text{Y}_2\text{Ba}_3\text{O}_6$ (below $p_{O_2} = 5 \cdot 10^{-5}$ Pa at 770 °C). Below $p_{O_2} = 10^{-9}$ Pa, only Cu and yttrium–barium oxides are stable at 770 °C as follows from the appropriate phase diagrams in Fig. 1.

![Diagram](https://ntrs.nasa.gov/search.jsp?R=19900018518)

**Figure 1.** Phenomenological presentation of equilibrium pseudoternary phase diagram $\text{Y}--\text{Ba}--\text{Cu}--\text{O}$, projected on the plane of the metallic components at 770 °C for low oxygen partial pressures $p_{O_2} = 5 \cdot 10^{-5}$ Pa (A) and $p_{O_2} = 10^{-9}$ Pa (B).
Since it is an inherent property of Ba to form very stable peroxide and carbonate, the possibility of substitution for oxygen by peroxide or carbonate anions can henceforth be considered in the Ba rich region of the phase diagrams. In Fig. 2, Y—Ba—Cu—O(CO₂) phase diagrams are drawn including approximate (kinetic) stability regions of the appropriate carbonates for 10⁵ Pa oxygen atmosphere (with < 1 ppm of CO₂). Such phase diagrams apply if, e.g., a limited amount of CO₂ is introduced into the system via BaCO₃.

**Figure 2.** Equilibrium phase diagrams Y—Ba—Cu—O(CO₂) for various maximal firing temperatures of carbonates-containing starting materials in 10⁵ Pa oxygen atmosphere with ≤ 1 ppm CO₂. Stability regions of the oxides—carbonates depicted (broken line).

As follows from the Fig. 2, the decomposition temperature of YBa₂Cu₃O₉₋δ—CO₂ (tetragonal, nonsuperconducting) is rather low, 830 °C (formation at a temperature as low as 750 °C is observed). The Ba—richer phase Ba₆Y₃₊xCu₄₊y(CO₃)₂O₁₀+η, with x ≤ 0.3, y ≤ 0.5 and η ≤ 3, decomposes at 960 °C into YBa₄Cu₃O₉₊ε (the phase is described in Ref. 5). With even higher Ba—content, Y₂Ba₃O₆—CO₂ (erroneously assigned as Y₂Ba₂O₅ in Ref. 13) decomposes at a temperature as high as 1080 °C.

Although of particular interest, no reliable data on substitution of oxygen by peroxygroups in the YBa₂Cu₃O₉₋δ could yet be obtained since determination of O²⁻ in the structure is rather ambiguous. A verified study using ¹⁸O labeling is described in Ref. 15. Samples prepared from BaO₂ in closed pressurized systems showed contraction of c axis and no high Tc superconductivity. Rietveld refinements of the powder neutron diffraction data for such samples indicate coordination of oxygen—containing, cluster—like species around the Cu(1) atom. However, no clear distinction can be made between peroxygroups and carbonate groups which possibly originate from adventing carbon in the used BaO₂. Nevertheless, no reaction with permanganate, otherwise readily proceeding with BaO₂, was observed in the YBa₂Cu₃O₉₋δ samples presumably containing the peroxygroups.

**Substitution for Ba and Y by rare earths.** A large variety of elements can, at least partially, be accommodated at the Y and Ba sites in the structure of YBa₂Cu₃O₉₋δ. Yttrium can be fully replaced by rare earths Yb—to—Dy and Gd, Eu and Sm. According to equilibrium firing experiments at 910 °C, followed by oxygen saturation at 340 °C, Lu and Tb replace Y up to 1/3. For Nd, Pr and La, an occupational equilibrium between the Y and Ba site exists, which means that the Ba site can accommodate the large rare earth. For Nd, the equilibrium favours occupation of the Y—site, whereas the Ba—site is preferred if La is involved. No substitution solely for Y can be reached using Nd and larger rare earths, neither can any substitution solely for Ba be obtained for Pr and smaller rare earth. If the former is attempted, the BaCuO₂₋ₓ impurity phase bounds the simultaneously replaced yttrium and emerges together with CuO. Only La is large enough as not to attack the Y—site unless it is present in the Ba—site in concentration higher than 35%. Then, Y is substituted by La as well and it emerges as Y₂Cu₂O₅. In Fig. 3, these situations are shown in pseudoquaternary
tetrahedral diagrams.

Figure 3. Relevant portions of the pseudoquaternary tetrahedral diagrams of the RE—Y—Ba—Cu—O phase system for RE = Nd and La after equilibrium firing at 910°C and oxygen saturation at 340°C. Note the surroundings of the (Y,RE)(Ba,RE)2Cu3O9−δ solid solution regions in the pseudopseudoternary cut.

As for cerium, this element does not substitute either Y or Ba more than a few %. Excess of Ce is bound into BaCeO3 (perovskite type; (Ba(Tb,Cu))O3 in case of Tb) and a (Ba,Ce,Y)2CuO4 (T-Type phase, Ref. 16) emerging together with BaCuO2 in ratios depending on the elemental composition of the overall mixture.

Substitution for Ba and Y by alkaline earths. Of all possible combinations, only Ca for Y and Sr for Ba substitutions are significant, and replacements up to 25 % and 35 % respectively can be reached. Above these limits, Y2BaCuO5 together with another yet unidentified phases in case of Ca and Y2BaCuO5 with Sr14Cu24O41 (Ref. 17) in case of Sr emerge as impurity phases. If substitution of Ca for Ba is attempted, no substitution for Ba takes place, but a portion of Y is replaced instead and Y2BaCuO5 together with unidentified Ca poly-nary oxides appear as impurities. If substitution of Sr for Y is attempted, virtually no replacement, (4 ± 4) %, is achieved, a portion of Ba is substituted instead, and BaCuO2 appears as impurity. The situation is depicted in Fig. 4.

Figure 4. Pseudopseudoternary diagrams of the M—Y—Ba—Cu—O system, M = Ca and Sr, at 910°C equilibrium firing and oxygen saturation at 340°C; MCu(O)—BaCu(O)—YCu(O) cuts.

Substitution for Ba and Y by alkali metals. Contrary to some reports, rather limited substitution by alkali metals into YBa2Cu3O6−δ is found, although various precautions were made to prevent evaporation of the alkali metal peroxides, which are readily formed in the system. At 850 °C, in saturated vapour of an extra added peroxide, no more than cca 8 % of Ba is replaced by Na, while possibly up to 4 % of Y being replaced simultaneously.
No substitution of Ba with elements similar in size, K-to-Cs, was accomplished for levels above 5-10%.

**Substitution for Cu by Li, Mg and 3-d elements.** Contrary to some other quaternary cuprates, a rather low solid solubility, up to some 3% is found for Li at the Cu-sites of YBa$_2$Cu$_3$O$_{9-x}$. Similar observations are done for Mg. Extended solid solubility is shown only by Fe and Co (20% and 30%, respectively), and Ni and Zn (5-10%). For the other 3d-elements the extent of the solid solubility coincides with the detection limits of the X-ray method (Guinier–Hägg focusing camera). It is estimated to be lower than 3% for Sc, Cr and Mn and below 1% for Ti and V. In the copper poor region of the corresponding phase diagrams, the neighbouring phases to YBa$_2$(Cu,M)$_3$O$_{9-x}$ are poly-nary oxides rich in the metal M, like BaSc$_2$O$_4$, Ba(Ti,Y)$_4$O$_9$ + TiO$_2$, etc.

**Superconducting properties.** The existence of 3-d homogeneity spaces adjacent to a YBa$_2$Cu$_3$O$_{9-x}$ line in five component (one impurity) equilibrium phase diagrams allows $T_c$ to change with up to three degrees of freedom in the compositional parameters (considering fixed field $H$ and current $I$). For an oxygen content defined by saturation at $10^5$ Pa, $T_c$ is a strongly decreasing function of any substitution for Cu, e.g., 14 K/% of substitution by Zn or Mg, and for Fe and Co above a 5% substitution level. 3.2 K/% Ni and 2 K/% Li. The same trend is found on partial replacing of Ba with a smaller element, e.g., 0.26 K/% substitution by Sr. If substitution for Y takes place, it affects the $T_c$ only in case where the substituting element alters the charge balance. $T_c$ is especially prone to higher-valent substituents of Y which will lower the hole concentration in the copper-oxygen network. Thus Ca for Y substitution lowers $T_c$ at a rate of $\sim 0.5$ K/% Ca, whereas Pr at a rate of at least $1$ K/% Pr. Similar results are observed for Tb.

The preparations of the variously substituted samples learn that the presence of some impurities, either in form of solid solutions or as phase admixtures, improves the sintering characteristics and resulting mechanical properties of the YBa$_2$Cu$_3$O$_{9-x}$ based products, leaving the $T_c$- and $I_c$-determinant effects negligible. It seems therefore feasible to optimize the mechanical properties of the superconducting cuprate materials by substituting them with various elements, even if these eventually produce impurity phases.

**References**