Lanthanide Substitution in $YBa_2Cu_3O_{9-\delta}$

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The substitution limits for various rare earth (RE) elements on the different metal sites in the $YBa_2Cu_3O_{9-\delta}$ structure have been investigated. Two- or multi-phase equilibria are studied at the solid-solution limits. For samples undergoing equilibration at 910 °C followed by oxygen saturation at 340 °C, Y is completely substituted by elements from the series Sm–Gd and Dy–Yb, whereas only about 1/3 of Y can be replaced by Tb and Lu. For Nd, Pr and La as substituents, an occupational equilibrium between the Y- and Ba-site exists. The substitution for Ba is favoured as the atomic size of the RE substituent increases. Substitution solely for Y cannot be accomplished by Nd or larger RE elements. Similarly, substitution solely for Ba cannot be achieved by Pr or smaller REs. Only La is large enough to avoid the Y-site, however, only under the additional condition that its occurrence at the Ba-site is lower than 36(2) %. Ce does not substitute for Y or Ba by more than a few percent. No substitution of Cu by the smallest REs, Lu and Tb^{IV}, is observed. The substitutional behaviour of a mixture of almost all REs on $YBa_2Cu_3O_{9-\delta}$ is also studied. In two-phase mixtures of $REBa_2Cu_3O_{9-\delta}$ and RE_2BaCuO_5, an unequal distribution of REs over the available sites for the RE elements is found. Small REs preferentially enter the phase RE_2BaCuO_5. Using RE mixtures as a starting material, the occupational equilibrium of La, Pr and Nd between the Y- and Ba-sites of $YBa_2Cu_3O_{9-\delta}$ must be taken into account by a proper composition of the reactant mixture in order to obtain phase purity. T_c is lowered by the presence of REs at the Ba-site and by the presence of Pr at the Y-site.

$YBa_2Cu_3O_{9-\delta}$ is in focus owing to its interesting superconducting properties at relatively high temperatures. In the crystal structure four metal sites (Y, Ba and two Cu) are potential candidates when substitution by another cationic element is considered. Different sizes and shapes apply to the individual sites of the metal sub-structure, which put conditions on the size, charge and electron configuration of the potential substituent.

The present study is restricted to rare earths (REs) as substituents. Their considerable span in size,[1] together with their ability to take different valency states, permit all the metal sites in the $YBa_2Cu_3O_{9-\delta}$ structure to be considered as possible hosts. A proper structural characterization of such substituted phases, together with information about their electrical and magnetic properties, will be helpful for obtaining a better understanding of how structural aspects influence the properties of the high-T_c materials. Moreover, such knowledge will certainly also be of economical interest, since it is feasible that this may lead to effective synthesis routes which utilize cheap rare earth mixtures instead of expensive pure yttrium compounds as starting materials.

In the $YBa_2Cu_3O_{9-\delta}$-type structure, the eight-coordinated "yttrium" site is easily occupied by the majority of the REs, (La, Nd, Sm, Eu, Gd, Dy, Ho, Er and Tm; Refs. 2–11). However, the reports for RE = Yb and Lu refer mostly to phase impure samples.[12–14] The highly oxidative environ-

ment in $REBa_2Cu_3O_{9-\delta}$ is reported[2,4,15] to prevent the formation of phases with RE = Ce, Pr, and Tb (i.e. REs which can take the oxidation state IV). Nevertheless, even for the most incompatible RE (= ^iRE) a partial solid solubility of the type $(^iRE,^cRE)Ba_2Cu_3O_{9-\delta}$ is reached in combination with a compatible RE (= ^cRE).[14,16–19] Full miscibility of two ^cREs on the Y-site is generally described.[16,20–24]

Alternatively, the large Ba-site and the small Cu-sites can provide the scenario for a more comprehensive substitution process. The larger REs (such as La) can substitute for Ba up to some 50 % (Refs. 25–35). On the other hand, the Cu-sites are susceptible to substitution by quite different elements, such as the 3d-metals or, e.g., Li, Mg, Ga and Al (Ref. 36 and references therein). The smallest REs, such as Lu or Sc, are also candidates for the latter type of substitution.

In this work the preferences of the various REs for substitution on the different metal sites are reported. On the basis of the results obtained, the substitution behaviour of multi-lanthanide mixtures and their effect on the superconducting properties are discussed.

Experimental

Syntheses. All samples were synthesized by the liquid mixing technique of citrate gels followed by preparation cycles involving rehomogenization, firing and controlled oxidation. The samples were prepared using reagent-grade starting materials: $La(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ (both

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Merck), Pr$_6$O$_{11}$ (3 N, American Potash & Chemical Corp.), Nd$_2$O$_3$ (3 N, Molycorp), Y$_2$O$_3$ (5 N, Megon), Tb$_4$O$_7$ and Yb$_2$O$_3$ (both 4 N, American Potash & Chemical Corp.), Lu$_2$O$_3$ (4 N, Product LTD) and Sc$_2$O$_3$ (4 N, for preparation see Ref. 37). Two different mixtures containing a large number of the rare earth oxide-hydroxides were used, viz. one described here as 'raw material' and one termed 'by-product', according to their occurrence in the yttrium oxide production of the company A/S MEGON, Norway; (after annealing, analyses showed that 1 mol of RE elements corresponded to 134.0(2) and 177.0(3) g of raw material and byproduct, respectively). Furthermore, BaCO$_3$ (reagent grade, Merck), CuCO$_3$·Cu(OH)$_2$·0.5H$_2$O (Riedel de Häen) and citric acid monohydrate (Fluka, reagent grade) were used as starting materials, together with distilled water.

Dried RE oxides (analysed RE mixtures) were dissolved in boiling concentrated solutions of citric acid, whereafter stoichiometric amounts of dry BaCO$_3$ and analysed basic copper carbonate, together with water, were added to the solution. The resulting clear citrate gel was dried at 180 °C. After milling and subsequent burning in air at 450 °C, the powder was pressed into pellets and heated at 910 °C for 20 h and at 340 °C for 16 h (intermediate cooling rate 2 °C h^{-1}) in a corundum boat placed inside a tube furnace. The furnace was continuously flushed with oxygen gas purified on CuO at 600 °C and on KOH at ambient temperature. The rehomogenizations were performed in an agate vibrational mill. (Slightly different temperature conditions used during the preparation of YbBa$_2$Cu$_3$O$_{9-\delta}$ are described in the text.)

Chemical analyses. The RE content, either as a sum in the mixtures or as individual elements, was determined complexometrically in a HCl solution buffered with urotropine at pH 3–5 using Xylenol Orange as indicator. The volumetric Na$_3$HEDTA solution (Merck) was standardized using ultrapure Sc(HCOO)$_3$; for preparation see Ref. 38. The invidual concentrations of the various REs in the mixtures were analyzed by ICP emission spectral analysis (Applied Research Laboratories instrument, calibration by commercial standards). The oxygen (and thus copper) content was determined iodometrically as described previously.[39]

Powder X-ray diffraction. All samples were characterized by powder X-ray diffraction (PXD) measurements using Guinier–Hägg cameras, Cu $K\alpha_1$ radiation and Si as internal standard. Positions and integrated intensities of Bragg reflections were obtained by means of a Nicolet L18 film scanner and using the SCANPI program system.[40] Unit cell dimensions were deduced by least-squares refinements,[41] using positions only for the $\sim$ 20 reflections which could unambiguously be indexed as non-overlapping lines. Quantitative analyses of the amounts of different phases were carried out based on comparisons of observed and integrated PXD intensities calculated by the LAZY-PULVE-RIX program.[42] The influence of various sample effects on the relative intensity of the Bragg reflections used for the quantitative phase analysis was tested with selected standard two-phase mixtures. The estimated accuracy in the product contents is ± 30 %, unless stated otherwise.

DC resistance and AC susceptibility measurements. The specimens were cut from sintered rods to approximate size 1.5×1.5×8 mm. Phosphor bronze contacts were used for the four-point measurements. The current was 5 mA or less (corresponding to a maximum current density of 2 kA m^{-2}) and was repeatedly reversed to eliminate thermoelectric voltages. The voltage was measured by a DVM having a 1 μV resolution. The samples were mounted in good thermal contact with a copper block, the temperature of which was measured with a resistance thermometer.

The AC magnetic susceptibility measurements were performed on cylindrical samples with diameter 6.5 mm and length 5 mm. Frequencies of 74 and 300 Hz were used. The in-phase and quadrature signals were converted into susceptibility by the use of Crabtree's values[43] for the demagnetization factor, evaluated on the basis of macroscopic dimensions without any correction for porosity. The experimental set-up was calibrated by a pure sample with a low demagnetization factor, assuming the internal susceptibility to be −1 at 4 K. Additional susceptibility measurements were carried out using a SQUID magnetometer (Quantum Design) for temperatures down to 2 K.

Results and discussion

(i) Pure YBa$_2$Cu$_3$O$_{9-\delta}$. For verification of the chosen conditions for syntheses and testing of the starting materials, blank experiments were carried out by preparing pure YBa$_2$Cu$_3$O$_{9-\delta}$. When dried (200 °C) BaCO$_3$, analyzed basic copper carbonate (115.64 g mol^{-1} Cu) and analyzed Y$_2$O$_3$ (99.87 %) were used, a more than 99 % phase-pure YBa$_2$Cu$_3$O$_{9-\delta}$ product was obtained, as judged from PXD analysis. The oxygen content was analyzed to 9 − δ = 6.96(1). The standard sample has unit cell dimensions a = 381.87(3), b = 388.59(3) and c = 1168.02(12) pm, which correspond to the highest attainable orthorhombic distortion under saturation at 1 atm O$_2$ pressure.

(ii) Complete substitution of Y with RE; REBa$_2$Cu$_3$O$_{9-\delta}$. By proceeding through the series of rare earths, a significant contraction of the atomic and ionic size occurs. For selected elements, the valency may depart from the usual +III value. In the present study we hence focus on the compatibility of the large REs (La, Ce, Pr and Nd), of the small REs (Yb, Lu and Sc) and of the potentially tetravalent REs (Ce, Pr and Tb), with respect to the YBa$_2$Cu$_3$O$_{9-\delta}$-type structure.

For the potentially tetravalent REs, no indication of a REBa$_2$Cu$_3$O$_{9-\delta}$-type phase was found for RE = Ce and Tb, whereas the Pr samples were virtually pure (see below). In the case of RE = Ce (Tb), the PXD diagrams showed three-phase mixtures containing BaCeO$_3$, or alternatively

Table 1. Total substitution of Y by RE (La, Pr, Nd) in $YBa_2Cu_3O_{9-\delta}$ attempted. Equilibrium compositions of resulting biphasic mixtures of $RE(Ba_{1-y}RE_y)_2Cu_3O_{9-\delta}$ and $BaCuO_{2+v}$. (Phase content in pseudoatom % concerning metal atoms; estimated error in $BaCuO_{2+v}$ content amounts ±20 % of value; equal Cu valency for both phases is assumed for calculation of 9–δ. Unit cell dimensions refer to main component; calculated standard deviations are in parentheses.)

RE	$BaCuO_{2+v}$ (%)	y	9–δ	a/pm	b/pm	c/pm
La	15	0.09(2)	7.05(1)	391.68(5)	–	1174.7(2)
Pr	8.5	0.05(1)	7.03(1)	386.36(6)	392.59(4)	1170.5(1)
Nd	5.5	0.030(5)	6.99(1)	386.14(5)	391.60(8)	1175.1(2)

Table 2. Partial (1/4) substitution of Y by RE (La, Pr, Nd, Ce) in $YBa_2Cu_3O_{9-\delta}$ attempted. Unit cell dimensions refer to this substituted phase; calculated standard deviations in parentheses.

RE	Composition of products[a] (pseudoatom %)		a/pm	b/pm	c/pm
La	92.8 % $(Y_{.81}La_{.19(2)})(Ba_{.961}La_{.039(9)})Cu_3O_{7.00}$	7.2 % $BaCuO_{2+v}$	383.06(6)	389.24(9)	1166.8(4)
Pr	97.1 % $(Y_{.77}Pr_{.23(1)})(Ba_{.985}Pr_{.015(3)})Cu_3O_{6.94}$	2.9 % $BaCuO_{2+v}$	382.86(4)	389.49(6)	1167.7(2)
Nd	98.6 % $(Y_{.76}Nd_{.239(4)})(Ba_{.993}Nd_{.007(2)})Cu_3O_{6.92}$	1.4 % $BaCuO_{2+v}$	383.14(4)	389.39(4)	1168.8(1)
Ce[b]	85.8 % $YBa_2Cu_3O_7$ 5 % $BaCuO_2$ 5 % $BaCeO_3$	5 % $(Ba,Ce)_2CuO_4$	383.8(2)	388.5(1)	1165.1(5)

[a]Estimated error in $BaCuO_{2+v}$ content, ±20 % of value, assuming no substitution of La for Ba (no change in unit cell volume observed). [b]The Ce substitution for Y and for Ba in the major phase is estimated as less than 3 %.

$BaTbO_3$ (for crystal structures, see Refs. 44 and 45) and $BaCuO_2$, together with CuO.

The attempted preparation of pure $REBa_2Cu_3O_{9-\delta}$ with the large REs, RE = La, Pr and Nd, resulted in samples containing a minor impurity of $BaCuO_{2+v}$. This impurity is, however, caused by a partial substitution of Ba with the RE, i.e. $RE(Ba_{1-y}RE_y)_2Cu_3O_{9-\delta}$. The tendency towards accommodation at the Ba-site increases with increasing size of the RE atom, thus being most pronounced for RE = La (Table 1). In order to obtain pure, single-phase samples, the composition of the starting mixture must be enriched in RE to compensate for the RE which occupies the Ba-site.

Attempts to prepare $REBa_2Cu_3O_{9-\delta}$ with the small REs were totally unsuccessful in case of RE = Sc and Lu. Instead, Lu_2BaCuO_5, $BaCuO_{2+v}$ and a hitherto unknown Lu-containing phase were formed in the case of RE = Lu, and $Ba_2Sc_2Cu_2O_7$,[46] $BaCuO_{2+v}$ and CuO in the case of RE = Sc. $YbBa_2Cu_3O_{9-\delta}$ has a reduced thermal stability compared to $YBa_2Cu_3O_{9-\delta}$. The peritectic decomposition temperature is lowered from 950 to $\sim 905\,°C$. Phase-pure samples for RE = Yb can be obtained via a multiple firing procedure, starting at $\sim 850\,°C$ with subsequent rehomogenizations and a gradual increase of the firing temperature. The unit cell dimensions of the obtained $YbBa_2Cu_3O_{6.965}$ are a = 380.33(4), b = 387.41(3) and c = 1166.45(12) pm.

(iii) Partial substitution of Y with RE; $(Y_{1-x}RE_x)Ba_2Cu_3O_{9-\delta}$. The apparent incompatibility of the largest, smallest and typically tetravalent REs with respect to the $YBa_2Cu_3O_{9-\delta}$-type structure does not exclude that partial miscibility between Y and these REs may be accomplished.

The largest REs partly substitute for Ba as well as for Y (see section ii), with $BaCuO_{2+v}$ appearing as the second

phase (Table 2). Among La, Pr and Nd, a different degree of preference for the Ba-site is observed. As an example, if 1/4 of Y is intended to be substituted by one of these REs, as much as 29 % of the introduced La goes to the Ba-site, whereas only 12 % of Pr and 6 % of Nd do so.

Cerium follows this pattern only partly, owing to its tendency to behave as a tetravalent element. (Note that Pr behaves as a trivalent element when it substitutes for Ba.) The substitution of Y (and Ba) by Ce is low. Thus the deficit of Y in, say, a nominal $Y_{0.75}Ce_{0.25}Ba_2Cu_3(O)$ mixture leads to the formation of additional phases containing Ce, Ba and Cu. Thus, approximately 5 pseudoatom % of each of $BaCeO_3$, $BaCuO_{2+v}$ and of $(Ba_{1-y}Ce_y)_2CuO_4$ are found. The latter adopts a structure related to the K_2NiF_4 type, with $a \approx 384$ and $c \approx 1361$ pm. According to the mole balance, which in this case is only approximate, the Cu substitution on both the Y- and Ba-site is less than 3 % (Table 2). The partial substitution is substantiated by comparison of the unit cell dimensions with those of the pure standard $YBa_2Cu_3O_{6.96}$.

Of the remaining, potentially tetravalent REs, Pr forms

Table 3. Unit cell dimensions of $(Y_{1-x}Tb_x)Ba_2Cu_3O_{9-\delta}$ (solubility limit x = 0.35 ± 0.05) and $(Y_{1-x}Lu_x)Ba_2Cu_3O_{9-\delta}$ (solubility limit x = 0.33 ± 0.07). Calculated standard deviations in parentheses.

RE	x	a/pm	b/pm	c/pm	9–δ
Tb	0.05	382.07(6)	388.52(6)	1167.4(2)	6.96
Tb	0.10	382.12(6)	388.69(6)	1168.2(1)	6.95
Tb	Saturated	382.6(1)	388.6(1)	1169.2(3)	–
Lu	0.10	381.76(4)	388.39(3)	1167.5(1)	6.97
Lu	Saturated	381.2(1)	388.1(2)	1167.4(7)	–

Table 4. Partial (1/8) substitution of Ba by RE (La, Pr, Nd, Ce) in $YBa_2Cu_3O_{9-\delta}$ attempted. Unit cell dimensions refer to this substituted phase; calculated standard deviations in parentheses.

RE	Composition of products[a] (pseudoatom %)				*a*/pm	*b*/pm	*c*/pm
La	100 % $Y(Ba_{.875}La_{.125})_2Cu_3O_{7.05}$				382.46(6)	387.86(6)	1162.2(2)
Pr	86 % $(Y_{.92}Pr_{.08})(Ba_{.90}Pr_{.10})_2Cu_3O_{7.02}$	9 % $(Y_{.96}Pr_{.04})_2BaCuO_5$	5 % CuO		385.80(5)	–	1163.4(2)
Nd	85 % $(Y_{.85}Nd_{.15})(Ba_{.94}Nd_{.06})_2Cu_3O_{7.01}$	10 % $(Y_{.94}Nd_{.06})_2BaCuO_5$	5 % CuO		383.04(7)	388.22(6)	1165.1(3)
Ce	71 % $YBa_2Cu_3O_{9-\delta}^b$	9 % $Y_2BaCuO_5^c$	13 % CuO	7 % $BaCeO_3$	382.40(6)	388.48(8)	1166.1(3)

[a]Estimated error in content of minor phases ± 10 % of the value, estimated error in Nd and Pr subsitution ± 20 % of the values.
[b]Substitution for Ba less than 1 %. [c]No shift in unit cell volume owing to substitution.

Table 5. Partial substitutions of Cu by RE = Tb and Lu in $YBa_2Cu_3O_{9-\delta}$ attempted at various nominal Cu/RE molar ratios (RE and ratio given). Unit cell dimensions refer to $(Y_{1-x}RE_x)Ba_2Cu_3O_{9-\delta}$; calculated standard deviations in parentheses.

RE; Cu/RE	Composition of products[a] (pseudoatom %)				*a*/pm	*b*/pm	*c*/pm
Tb; 29	91 % $(Y_{.98}Tb_{.02})Ba_2Cu_3O_{9-\delta}$	7 % $(Y_{.98}Tb_{.02})_2BaCuO_5$	3 % $BaTbO_3$ [b]		382.5(1)	388.5(2)	1166.4(7)
Tb; 9	82 % $(Y_{.92}Tb_{.08})Ba_2Cu_3O_{9-\delta}$	11 % $(Y_{.92}Tb_{.08})_2BaCuO_5$	6 % $BaTbO_3$ [b]		382.3(1)	388.4(1)	1167.7(4)
Tb; 5	70 % $(Y_{.93}Tb_{.07})Ba_2Cu_3O_{9-\delta}$	12 % $(Y_{.93}Tb_{.07})_2BaCuO_5$	14 % $BaTbO_3$	4 % CuO	382.7(1)	388.4(1)	1167.3(2)
Lu; 29	93 % $(Y_{.91}Lu_{.09})Ba_2Cu_3O_{9-\delta}$	6 % $(Y_{.89}Lu_{.11})_2BaCuO_5$	0.6 % $BaCuO_{2+v}$		382.2(1)	388.6(1)	1165.8(4)
Lu; 9	81 % $(Y_{.79}Lu_{.21})Ba_2Cu_3O_{9-\delta}$	16 % $(Y_{.73}Lu_{.27})_2BaCuO_5$	3 % $BaCuO_{2+v}$		382.1(1)	388.4(1)	1166.3(3)
Lu; 5	49 % $(Y_{.74}Lu_{.26})Ba_2Cu_3O_{9-\delta}$	35 % $(Y_{.65}Lu_{.35})_2BaCuO_5$	16 % $BaCuO_{2+v}$		381.9(1)	388.1(1)	1168.2(3)

[a]Degree of Tb for Y substitution considered equal for both phases. Degree of Lu for Y substitution in Y_2BaCuO_5-type phase estimated on the basis of the Vegard rule. [b]CuO should be present in small amounts, but is not observed.

a complete solid solution phase, section (ii), whereas Tb substitutes Y up to a level of 35(5) %. Above this level, the excess Tb enters into $Ba(Tb_{1-z}Cu_z)O_3$,* with CuO and $BaCuO_{2+v}$ as additional phases. The unit cell dimensions of $(Y_{1-x}Tb_x)Ba_2Cu_3O_{9-\delta}$ are listed in Table 3.

Y can be completely substituted by the smaller rare earths, Dy–Yb, but a rather limited solubility is found for Lu and Sc (Table 3). Lutetium substitutes yttrium up to 33(7) % as compared with the estimate of ~ 50 % in Ref. 47. Attempts to obtain higher substitution levels lead to the excess of Lu entering into a yet unidentified Cu-rich phase, which coexists with an Y_2BaCuO_5 type phase and $BaCuO_{2+v}$. Scandium shows a very low compatibility with the Y-site of the $YBa_2Cu_3O_{9-\delta}$ type structure and the extent of the solid solution interval is less than 4 % The Sc-saturated phase has the unit cell dimensions $a = 382.0(1)$, $b = 389.0(1)$, $c = 1168.0(4)$ pm. If a substitution level higher than 4 % Sc for Y is attempted, the excess Sc enters into a $Sc_2Ba_2Cu_2O_7$ type phase, accompanied with $BaCuO_{2+v}$ and probably CuO (below the detection limit at low scandium contents).

(iv) Partial substitution of Ba with large RE = La, Ce, Pr and Nd; $Y(Ba_{1-y}RE_y)_2Cu_3O_{9-\delta}$. As discussed above, the larger REs exhibit a clear preference to substitute for Ba. In the case of La, phase-pure $Y(Ba_{1-y}La_y)_2Cu_3O_{9-\delta}$ may be obtained up to $y = 0.36(2)$.[†] However, this simple beha-

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* Solid solutions are readily formed, e.g. $BaTb_{0.75}Cu_{0.25}O_{2.78}$ exists with $a = 605.2(3)$ pm and $\alpha = 60.04(6)°$.
[†] Estimated from the product phases using the principle of mole balance.

viour is not found for the smaller Pr and Nd (Table 4). When, say, 1/8 of the Ba is intended to be substituted by Pr or Nd, 69 % of Pr and only 42 % of Nd is actually found to enter the Ba-site. Subsequently, 28 % of Pr or 53 % of Nd enter into the Y-site while 3 % of Pr or 5 % of Nd are bound into a solid solution $(Y_{1-x}RE_x)_2BaCuO_5$ which emerges, together with CuO, as accompanying phases. The composition of the $(Y_{1-x}RE_x)_2BaCuO_5$ solid solution (Table 4) was estimated assuming the validity of the Vegard rule. The unit cell volumes of the nonexistent Pr and Nd analogues were extrapolated as 0.545 and 0.532 nm^3, respectively, on the basis of values for the Sm-to-Yb compounds in Ref. 48. For RE = Ce, the situation is even more complex, and upon attempts to produce $Y(Ba_{1-y}Ce_y)_2Cu_3O_{9-\delta}$, a four-component equilibrium mixture of $BaCeO_3$, CuO, $YBa_2Cu_3O_{9-\delta}$-type and Y_2BaCuO_5-type phases is obtained.

Phase diagrams, showing the solid-solution regions of $(Y_{1-x}RE_x)$ $(Ba_{1-y}RE_y)_2Cu_3O_{9-\delta}$ for RE = La, Pr and Nd are given in Fig. 1. It can be seen that attempts to substitute the largest atom La for Ba at a higher level than $y = 0.36(2)$ lead to a parallel substitution for Y (viz. $x > 0$ in the above formula) and in turn to the formation of $Y_2Cu_2O_5$. On the other hand, for all attempted x, La cannot substitute for Y without simultaneously attacking the Ba-site. Neither can Pr or Nd, in spite of the fact that the decreasing RE size makes accommodation on the Ba-site less favourable and that on the Y-site more preferable. Sm is the first element in the RE series that is sufficiently small to be exclusively accommodated at the Y-site without replacing barium. It should be mentioned that metastable phases with much
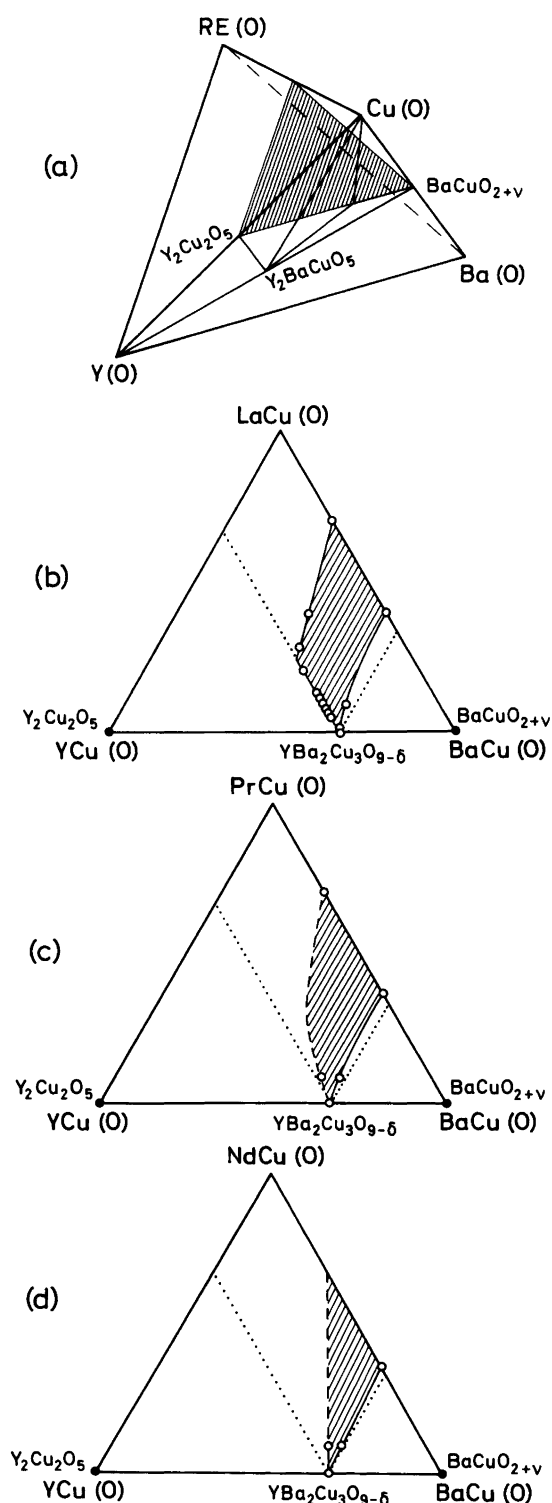
Fig. 1. $(Y_{1-x}RE_x)(Ba_{1-y}RE_y)_2Cu_3O_{9-\delta}$ solid solutions in a pseudo-quaternary tetrahedral phase diagram of Y–RE–Ba–Cu(O) as observed for samples fired at 900 °C and saturated in oxygen at 340 °C. (a) Position of the relevant cut (shaded) at 50 mol % Cu (metal atoms only). The particular cuts with regions of solid solubility (shaded) are shown for RE = La (b), and phenomenologically for RE = Pr (c) and RE = Nd (d). (No projections from Cu-richer and Cu-poorer parts of the tetrahedron are drawn. Open circles represent experimental points; for accuracy see Tables 1,2 and 4.)

smaller REs as substitutents for Ba can be prepared by the citrate gel technique using low firing temperatures (~ 800 °C).[49] According to our observations, the products thus obtained show rather diffuse PXD patterns with tetragonal symmetry. It is in fact possible that these phases are stabilized by CO_3^{2-}.

(v) Partial substitution of Cu with small RE = Tb^{IV}, Lu^{III} and Sc^{III}; $YBa_2(Cu_{1-z}RE_z)_3O_{9-\delta}$. According to XANES data,[50] no Ho/Cu disordering is observed in $HoBa_2Cu_3O_{9-\delta}$. Since the ionic size for six-coordinated Ho^{3+} is as large as 89 pm,[1] the smallest RE ions, viz. Lu^{3+}, Tb^{4+} and Sc^{3+} (85, 76 and 73 pm, respectively), may still be interesting candidates for substition at the Cu-sites. However, no phase-pure products could be achieved for Tb- and Lu-substituted samples of this type (Table 5). As follows from mole balance calculations, the substitution limits of Tb and Lu are 0(3) and 0(2) %, respectively. Only Sc was found to substitute for Cu, yielding phase-pure samples, but only up to the rather minor level of ~ 1 % substitution.[36]

(vi) Rare earth distribution between $REBa_2Cu_3O_{9-\delta}$ and RE_2BaCuO_5, RE = $Sm-Lu$. Under the chosen preparation conditions, RE_2BaCuO_5 phases are the only RE-containing phases to appear in equilibrium with $REBa_2Cu_3O_{9-\delta}$. For RE = Sm–Lu, RE_2BaCuO_5 takes an orthorhombic struc-
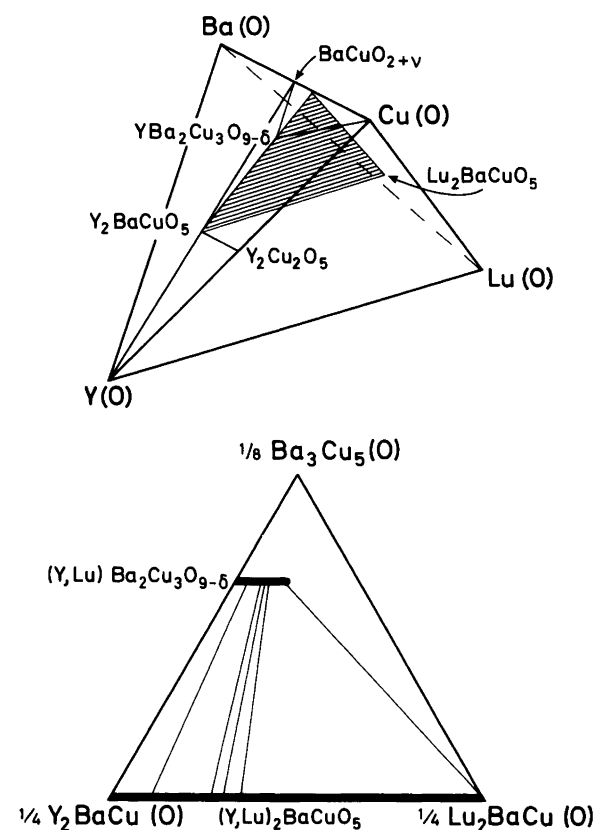

Fig. 2. Distribution of Y and Lu between $(RE)_2BaCuO_5$ and $REBa_2Cu_3O_{9-\delta}$ in two-phase equilibrium mixtures.

ture,[51] whereas for RE = La–Nd, a different, tetragonal structure[52] occurs which exhibits a certain degree of mutual substitution between the Y- and Ba-sites.[53] Together with the partial La (Pr, Nd) replacement for Ba in $REBa_2$-$Cu_3O_{9-\delta}$, this makes any RE distribution equilibria very complex in systems exclusively containing the largest REs. Therefore, only the two-phase systems involving the smaller REs which form the orthorhombic RE_2BaCuO_5-type structure are considered here. Three different sites for REs are then altogether available in the two-phase mixture. If two or more RE elements are present, an unequal RE distribution among these sites may be expected, involving both intra- and interphase equilibria. Generally, the smaller REs show a tendency to prefer accommodation in RE_2BaCuO_5, whereas the larger ones prefer $REBa_2$-$Cu_3O_{9-\delta}$, as illustrated by the Y/Lu pair in the equilibrium phase diagram presented in Fig. 2.

(vii) Substitutions in $YBa_2Cu_3O_{9-\delta}$ using lanthanide mixtures. The two basic sources used in the preparation of multi-substituted $YBa_2Cu_3O_{9-\delta}$ samples are the raw material and the byproduct of the industrial production of pure Y_2O_3 mentioned in the experimental section. These sources contain virtually all the REs. The RE contents in these sources were analyzed prior to synthesis (see the experimental section).

In Fig. 3 the percentage distributions of the REs in the raw material and in the byproduct are shown according to their ionic size[1] for coordination number eight. The size span is as large as 20 %. In (inter)metallic phases, a common criterion for the occurrence of extensive solid solutions is that the solute and solvent atoms should not differ

by more than 15 % in size (the Hume–Rothery rule). However, the $YBa_2Cu_3O_{9-\delta}$ phase cannot be considered as an ordinary metal in this respect, since directional bonding is definitely of importance. This has recently been taken into account in computer simulations[54] of substitutions, based on energy minimization according to a polarized ionic model, and, curiously, the calculated energies also change by some 20 % from La to Lu. Thus, a rather high accommodative ability of the Y-site is implied by the existence of the $YBa_2Cu_3O_{9-\delta}$-type phase for the REs La–Yb. The similarity in size between Ba and the larger REs explains the occurrence of RE substitution for Ba (e.g. $r_{La^{3+}}$ is 81 % of $r_{Ba^{2+}}$ for coordination number ten). However, such arguments would clearly favour substitution of Cu by the smaller REs (e.g. for coordination number six, $r_{Cu^{2+}}$ and $r_{Lu^{3+}}$ differ by 14 %, while $r_{Cu^{2+}}$ and $r_{Tb^{4+}}$ differ by only 4 %), but the existence of strong directional bonding at the Cu-sites (linear/square-planar or square-pyramidal coordinations) implies that the coordination polyhedra offered are highly unfavourable for the REs.

It is obvious from the earlier discussion that the equilibrium situation for a $REBa_2Cu_3O_{9-\delta}$ sample, synthesized from the RE mixtures, must be complex, since some REs will prefer solely the Y-site, while others will be distributed over the Y- and Ba-sites, and Sc as substituent may even have a small affinity for the Cu-sites. In order to approach the synthesis of phase-pure samples starting from the raw material or the byproduct, samples with nominal compositions on the RE_2BaCuO_5 – $REBa_2Cu_3O_{9-\delta}$ line in the pseudoternary phase diagram were prepared (including samples corresponding to extrapolation along this line to negative amounts of RE_2BaCuO_5).

Samples prepared from the raw material and the byproduct showed different distributions of product phases. The raw material-based samples were obtained fairly phase pure ($\leq$ 1.5 pseudoatom % impurities) for the stoichiometric $REBa_2Cu_3O_{9-\delta}$ composition. The byproduct-based samples could only be obtained phase pure when the nominal composition was shifted 2.5 pseudoatom % towards Y_2BaCuO_5. The necessity of enriching the starting components with respect to the RE to obtain pure samples (thus confirming that this was not an artifact originating from an erroneous determination of the RE content in the starting materials) was ascertained by thorough analysis of all the components in blank experiments [section (i)].

Mole balances (Table 6) indicate that for the samples enriched progressively in REs, both the Ba- and the Cu-sites were subjected to an increasing degree of substitution. The Ba-site accommodates a portion of the larger REs and the Cu-site(s) were first believed to host the smallest RE, viz. Lu.[55] However, a subsequent complete ICP analysis of the byproduct showed the presence of as much as 10 wt. % TiO_2, besides small amounts of Mg (0.24 %), V (0.03 %) and Fe (0.02 %) which may all partly substitute for Cu.[36] Both the substitutions for Cu and the RE for Ba substitution cause a decrease in orthorhombic distortion as a structural effect.[36,56] The substitutions therefore account for
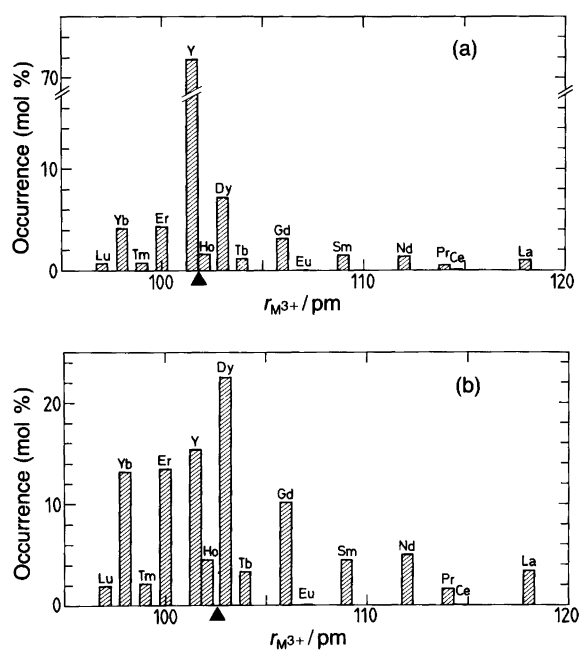

Fig. 3. Distribution (mol %, average marked by a lever point) of rare earths in (a) raw material and (b) byproduct.

Table 6. Substitutions caused by using the byproduct as a source of RE. Nominal compositions along the $(RE)_2BaCuO_5$ $-REBa_2Cu_3O_{9-\delta}$ tie line expressed in pseudoatom % (p) of the latter phase (referring to metal atoms only). Degree of substitution for Ba and Cu in $REBa_2Cu_3O_{9-\delta}$ given.

p (%)	Product distribution (pseudoatom %)			Substitution degree (%)	
	$BaCuO_{2+v}$	$(RE)_2BaCuO_5$	$REBa_2Cu_3O_{9-\delta}$	For Ba	For Cu
100	1.1	–	98.9	0.5	–
97.5	–	–	100	2.5	1.25
95	0.8	1.7	97.5	3.8	1.7
92.5	1.2	2.6	96.2	5.7	2.5
90	1.4	5.2	93.4	5.9	2.6

the observed crossover from orthorhombic to tetragonal structure of the $YBa_2Cu_3O_{9-\delta}$-type phase in the byproduct-based samples when using an excess of this starting material. The crossover occurred when the equilibrium (not nominal) phase mixture contained some 2.5 pseudoatom % of the Y_2BaCuO_5-type phase and some 1 pseudoatom % of $BaCuO_{2+v}$, corresponding to $\sim$ 4 % substitution of the Ba-site (viz. by large REs) combined with $\sim$ 2 % substitution of the Cu-site (by Mg, Ti and other d-metal impurities), cf. Fig. 4 and Table 6. The increasing presence of the smaller REs at the Y-site of RE_2BaCuO_5 is manifested by a decrease of the unit cell volume. Furthermore, the decrease

Fig. 4. Variation of unit cell dimensions of $BaCuO_{2+v}$-, Y_2BaCuO_5- and $YBa_2Cu_3O_{9-\delta}$-type phases as found for different samples synthesized from the RE byproduct mixture. Nominal starting compositions p, along the $REBa_2Cu_3O_{9-\delta}$–$(RE)_2BaCuO_5$ tie line, expressed in pseudoatom % of $REBa_2Cu_3$ (viz. referring to metal atoms only).

in the unit cell dimension c of $REBa_2Cu_3O_{9-\delta}$, as well as the decrease in the unit cell volume of the $BaCuO_{2+v}$ phase, are consistent with increasing substitution at their Ba-sites by the larger REs.

(viii) Superconducting properties. Since T_c of the $YBa_2Cu_3O_{9-\delta}$-type phase decreases both with RE substitution at the Ba-site[57] and with d-metal substitutions at the Cu-sites,[36] T_c is lowered for the products based on the RE mixtures. The pure $YBa_2Cu_3O_{9-\delta}$ becomes superconducting below T_c = 92(1) K, the sample based on the raw material has T_c = 91(1) K, and the byproduct-based sample has T_c = 84(1) K. The decrease is accounted for by a combination of all the variable substitution processes described in sections (iii)–(vii), but one significant detrimental substitutional effect arises here in addition because it specifically affects T_c. This is the incorporation of the potentially tetravalent REs, such as Ce and Pr. Their content in the byproduct starting material mixture amounts to 0.1 and 1.6 mole %, respectively, but the Pr content in the $YBa_2Cu_3O_{9-\delta}$-type phase of the product is increased by the interphase occupational equilibria. Notably, no decrease in T_c was observed in the phase-pure samples with Tb substituted for Y. The detrimental effect of Pr on T_c does not depend on whether Pr is present at the Y- or Ba-site. This was demonstrated by substituting separately Y and Ba in $YBa_2Cu_3O_{9-\delta}$ by an equal amount of Pr, say a fraction of 0.25 per formula unit. The composition of the resulting products has adjusted itself according to the equilibrium distribution of Pr between the Y and Ba sites (Tables 2 and 4). The phase with Pr substituted for Y (Table 2) contains 0.25 Pr per formula unit and has T_c = 67(1) K. The phase with Pr substituted for Ba (Table 4) contains 0.28 Pr per formula unit and has T_c = 59(1) K.

Different mechanisms may be attributed to the detrimental effect on T_c of the various substitution processes. The tetravalent rare earths decrease T_c via a decrease of the concentration of hole charge carriers, the large REs via a structural contraction (as is discussed in Ref. 57) and the d-metal impurities mostly via a change of the electronic configuration at the Cu-sites. As a result, removal of selected REs is recommended if RE mixtures are to be used for the production of this type of superconducting material.
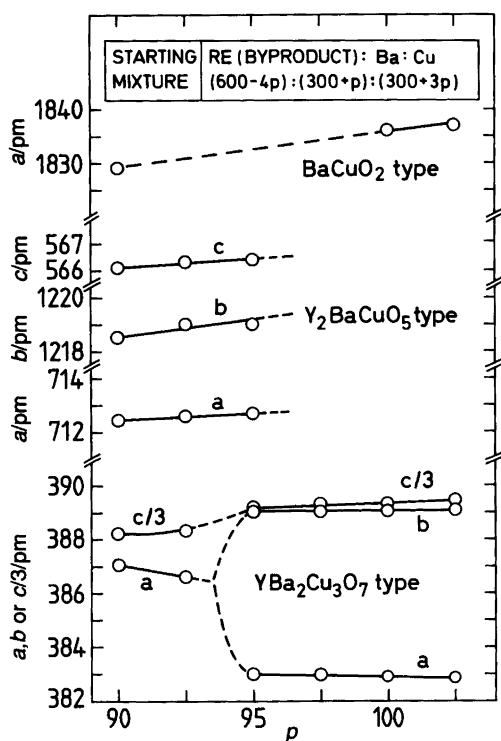
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