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Calcium-substituted Y-Ba-Cu-O superconductors with enhanced T_c synthesized at elevated oxygen pressures

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Calcium substitution in the Y-Ba-Cu-O system at elevated $P(O_2)$ results in superconducting compounds with novel and enhanced properties: tetragonal $Ca_xY_{(1-x)}Ba_2Cu_3O_y$ with $T_c=86$ K for $x=0.2$ prepared at $P(O_2)=16$ bars, and $Ca_xY_{(1-x)}Ba_2Cu_4O_y$ (1:2:4) with $T_c=89$ K for $x=0.1$ prepared at 50–200 bars. Calcium substitution shifts the phase-stability boundary between 1:2:3, 2:4:7, and 1:2:4 phases to higher $P(O_2)$, and stabilizes a tetragonal 1:2:3 structure at moderately elevated $P(O_2)$ *without* substantial decrease in T_c. The T_c of 1:2:4 increases with Ca substitution up to $x=0.1$, and then decreases gradually for larger x, possibly because of excessive hole concentration.

INTRODUCTION

Following the synthesis of a series of new 1:2:4 and 2:4:7 R-Ba-Cu-O superconductors in this laboratory,[1-3] we have been investigating the effect of chemical substitutions in these compounds. In this paper we report the results of the substitution of calcium in the Y-Ba-Cu-O system prepared at elevated oxygen pressures (16–200 bars).

Two considerations motivated this attempt at nonisovalent substitution of Ca^{2+} in place of Y^{3+}: (1) partial substitution of Ca for Y in 1:2:4 to give $Ca_xY_{(1-x)}Ba_2Cu_4O_y$ would increase the hole concentration from 1 to $(1+x)$ per formula unit if the oxygen content y remained at eight as in the parent 1:2:4 compound. By this means one could attempt to optimize the hole concentration to achieve the highest T_c. In this connection, it should be noted that compared to the chain oxygen in 1:2:3, the double chain oxygen in 1:2:4 is more tightly bound and so it is expected to maintain nearly the constant value of 8 under varying oxidation conditions. (2) When a 2+ ion replaces a 3+ ion in the compound, the oxygen content would be smaller at the same formal average copper valency (FACV). The oxygen that must be added to reach eight per formula unit will be greater, and the binding energy of the added oxygen should decrease; thus, one may need a higher oxygen pressure to form the 1:2:4 structure in preference to 1:2:3. The same argument would hold for 2:4:7 since it contains 1:2:4 layers. In other words, on Ca substitution, one may expect to see a shift in the 1:2:3-2:4:7-1:2:4 phase stability boundaries to higher $P(O_2)$ in the P-T-composition diagram.

SAMPLE PREPARATION

Samples were prepared by solid-state reaction of a stoichiometric mixture of Y_2O_3, BaO_2, CaO, and CuO, following the procedure described in Refs. 2 and 3. Compositions were prepared with metal ratios Ca:Y:Ba:Cu$=x:(1-x):2:3.5$ with $x=0$, 0.1, 0.2... 1.0 at intervals of 0.1. Each tablet was wrapped in gold foil and heated at 930°C at pressures of 16, 50, 100, or 200 bars in a commercial high-pressure oxygen furnace.[4] The duration of the heating was 14 h at the dwell temperature, followed by cooling at about 5 °C/min to room temperature. Each pellet was then reground and fired a second time under the same conditions. In a second series of experiments, additional samples were prepared at pressures of 50 and 100 bars at closer intervals of x ($x=0.075$, 0.09, 0.10, 0.11, 0.125, and 0.15) with metal ratios [Ca+Y]:Ba:Cu$=1:2:4$.

The sample tablets (after abrading the top surface) were examined by x-ray powder diffraction (XRD) on a Siemen's D500 diffractometer using Cu $K\alpha$ radiation filtered through a Ni filter. The detector slit width and the step size were both 0.05°. Using the available software, the $K\alpha_2$ peaks were removed and the background was subtracted. The observed "d" values were assigned to different phases by comparison with the known standard patterns, and the weight percent of the different phases were estimated by comparing the intensities of selected strong nonoverlapping lines.

PHASE DIAGRAM

For $x=0$, and synthesis temperature of 930 °C, the stable phase is 1:2:4 in the entire pressure range of 16–200 bars. This is consistent with our previous reported results.[1-3] However, on calcium substitution, the stable superconducting structure becomes 1:2:4, 2:4:7, orthorhombic 1:2:3, or tetragonal 1:2:3, depending on the calcium concentration and the oxygen pressure used during synthesis. Approximate phase diagrams are presented in Fig. 1. The estimates of phase concentration are approximate but are good enough to show the general features. At 16 bars, for small calcium concentrations ($x<0.15$) some 2:4:7 is formed but the predominant phase is calcium doped *tetragonal superconducting* 1:2:3, abbreviated CaT-123 [Fig. 1(a)]. For $x=0.2$ one finds nearly single-phase CaT-123. For larger x, a $BaCuO_2$-type second phase is found in the XRD, increasing

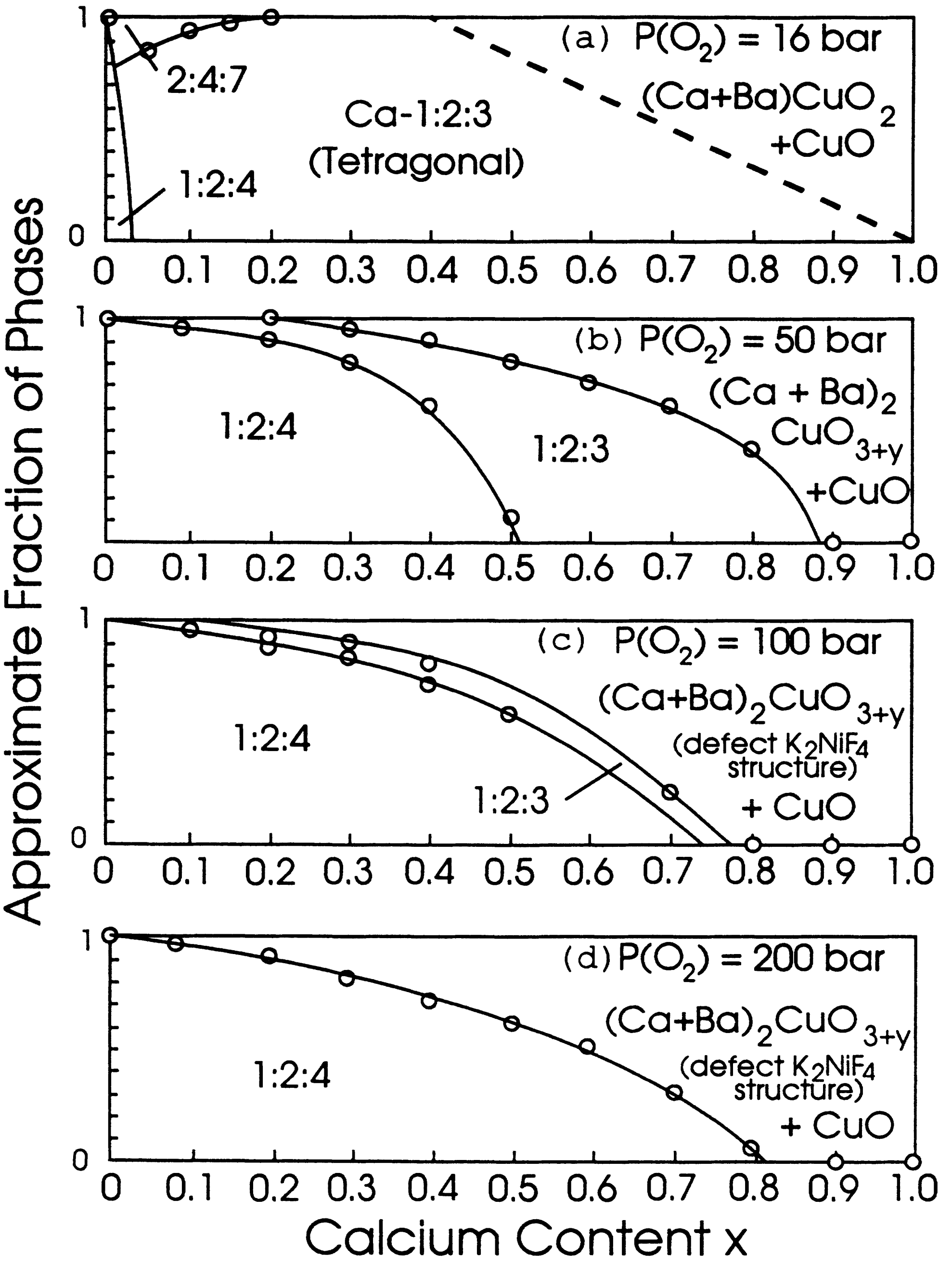

FIG. 1. Phases formed in the Ca-Y-Ba-Cu-O system with various fractions x of Ca substituted for Y, upon heating to 930 °C under oxygen pressures of (a) 16 bars, (b) 50 bars, (c) 100 bars, and (d) 200 bars. Approximate weight fractions are given based on comparison of XRD peak intensities. At 16 bars and $x > 0.05$, the principal superconducting phase is tetragonal 1:2:3, with T_c up to 86 K at $x = 0.2$. At 50 bars and above, orthorhombic 1:2:4 (and 1:2:3) are found, with T_c enhanced to 89 K for $x \approx 0.1$.

with x.

For higher pressures, (50–200 bars) the 1:2:4 obtained at $x = 0$ is also the majority phase for higher values of x [Figs. 1(b)–1(d)] but single phase 1:2:4 is obtained only for small x(< 0.10). The 1:2:4 phase disappears for $x > 0.8$ [Figs. 2(b)–2(d)]. A fraction of 1:2:3 is also found at higher x, but decreases at higher pressure; at 200 bar no 1:2:3 is seen. With increasing x a nonsuperconducting phase appears along with CuO, as indicated by additional XRD peaks. The positions and relative intensities of these additional peaks do not change noticeably with x from $x = 0.5$ up to the terminal phase at $x = 1$ (nominal composition 1 Ca+2 Ba+3.5 Cu). We identify this phase as $(Ca+Ba)_2CuO_{3+y}$, which is isostructural with K_2NiF_4 but with vacant oxygen sites. Although T_c changes with x, showing that the Ca content of the superconductor is changing to some extent, the positions of the 1:2:4 peaks as well as those of the

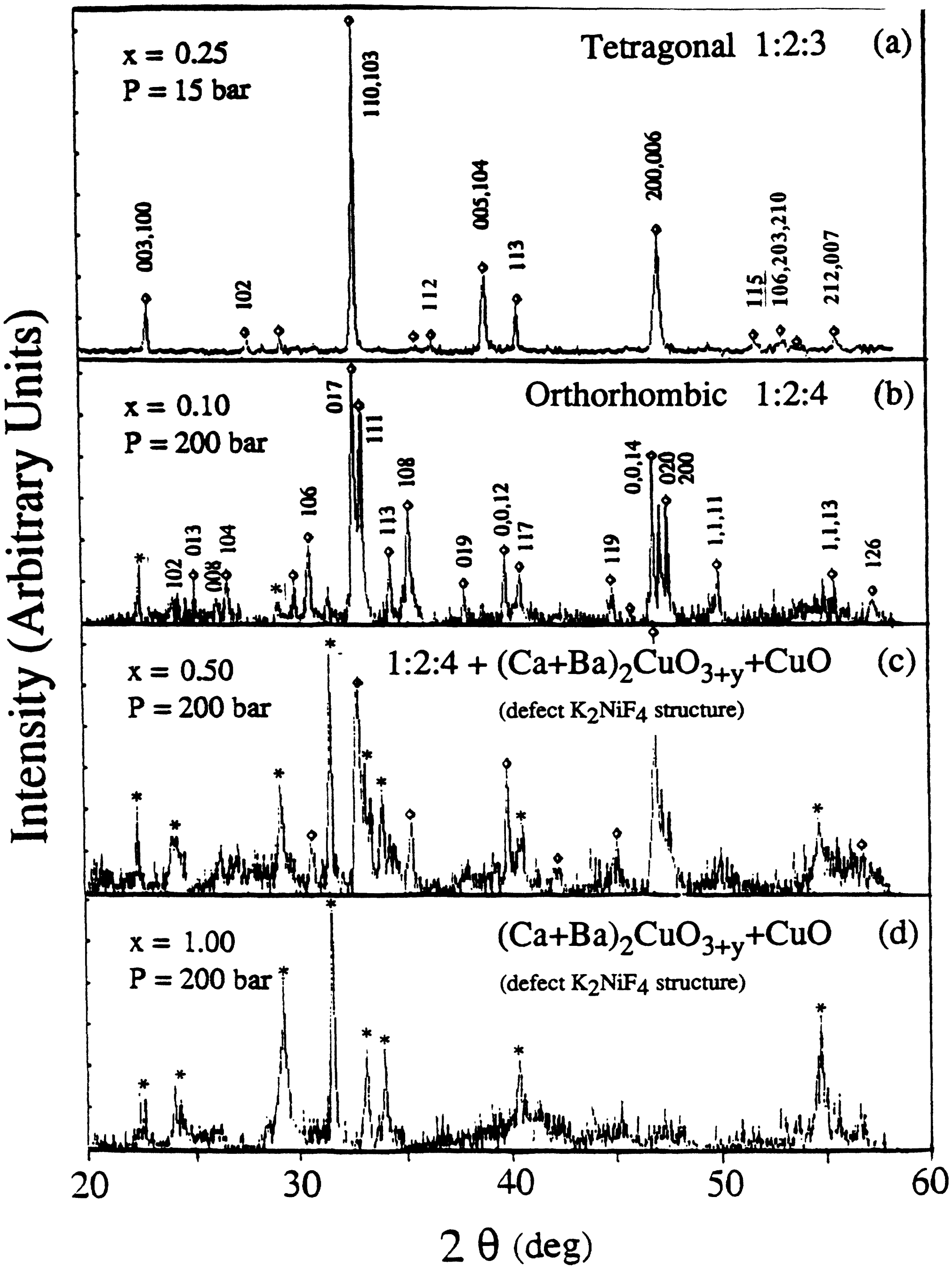

FIG. 2. X-ray powder diffraction patterns for four samples from Fig. 1. (a) Tetragonal superconducting 1:2:3 obtained for $x = 0.25$ at $P = 16$ bars. (b) Orthorhombic 1:2:4 obtained for $x = 0.1$ at $P = 200$ bars. The 1:2:4 lines have been assigned their *hkl*'s. (c) Ortho 1:2:4 obtained with $x = 0.5$ at $P = 200$ bars showing a significant amount of nonsuperconducting $(Ca+Ba)_2CuO_{3+y}$ isostructural with K_2NiF_4 (peaks marked with asterisk) found in all samples with large x prepared at $P \geq 50$ bars. (d) Pattern of the end member nonsuperconducting phase $Ca_{0.67}Ba_{1.33}CuO_{3+y}$ ($x = 1.0$, $P = 200$ bars).

$(Ca+Ba)_2CuO_{3+y}$ peaks shift less than 0.01° over this range of starting compositions, as determined by the peak search program of the diffractometer.

From Fig. 1, it is clear that calcium substitution does indeed shift the phase boundaries to higher pressures and tends to stabilize the 1:2:3 phase. Also, the 2:4:7 phase is absent. Another interesting observation is that although the nonsuperconducting phase formed at low pressures is of the $BaCuO_2$ type, this is replaced by $(Ca+Ba)_2CuO_{3+y}$ with the K_2NiF_4 structure at high $P(O_2)$ pressures (50 bars and above). This phase is favored at high $P(O_2)$ because it has four oxygen sites per unit cell, one of which is vacant at $y = 0$ and can be partly filled in high $P(O_2)$, raising the Cu valence above

2. As a result, at a given starting composition, the proportion of this nonsuperconducting phase increases with pressure.

SUPERCONDUCTING TRANSITION TEMPERATURES

Superconducting transitions were determined from Meissner diamagnetic susceptibility while cooling in a 20 Oe field using a Quantum Design SQUID magnetometer. The T_c (diamagnetic onset), transition width, and low-temperature diamagnetic moment change with calcium substitution (see the following). Unfortunately, interpretation of the results is complicated even for small values of x $(x<0.2)$ by the presence of a small amount of a second phase (1:2:3 for $P \approx 16$ bars, and the nonsuperconducting phase for $P > 50$ bars). In view of the uncertainty in the distribution of calcium over the two phases, the calcium content of the superconducting phases is not precisely known. However, the progressive shift in T_c shows that some further calcium substitution *is* taking place in the 1:2:4 structure. The exact concentration and site location are under investigation. In the following discussion, we therefore talk only in terms of the starting composition, keeping in mind the implicit limitation just mentioned.

A. Ca substituted tetragonal 1:2:3 (CaT-123)

Magnetization curves for samples prepared at 16 bars are shown in Fig. 3(a). In samples with $x=0.05$ and 0.15, we see two transition temperatures; presumably the higher one corresponds to the tetragonal 1:2:3 and the lower to the 2:4:7 phase. At $x=0.20$ and 0.25, the 2:4:7 phase disappears and we have a single superconducting phase, *tetragonal* 1:2:3, with $T_c \approx 86$ K (diamagnetic onset). It is interesting that the T_c of the tetraganal 1:2:3 phase is nearly as high as that of orthorhombic 1:2:3. This is in striking contrast to the formation in 1 bar O_2 of *orthorhombic* calcium substituted 1:2:3 reported by several researchers[5,6] who found T_c decreasing progressively to ~80 K at a solubility limit $x \approx 0.2$. Xiao *et al.*[7] found that partial gallium substitution for copper gave tetragonal 1:2:3 with a T_c of 65–80 K. Our results confirm that high T_c in 1:2:3 does not require orthorhombic distortion; the low T_c observed in unsubstituted tetragonal 1:2:3 is due to oxygen deficiency.

Previous authors,[5,6] have assumed that Ca^{2+} replaces Y^{3+} in O 1:2:3. This is expected from considerations of ion sizes, and the known preference of Ca^{2+} for a similar coordinate in bismuth and thallium superconductors. We extend this assumption to the Ca substituted 1:2:3 and 1:2:4 phases as well. To cause nonisovalent doping it is sufficient that the number of divalent ions (Ca+Ba) increases at the expense of trivalent Y, with either Ca or Ba entering the Y site. Otherwise, excess CuO, Ca, and/or BaO or $BaCuO_2$ would be left over to form a second phase. Consider a sample with initial cation ratios 0.25 Ca: 0.75 Y: 2 Ba: 3.5 Cu with the XRD pattern given in Fig. 2(a). If Ca did not replace Y, nearly $\frac{1}{4}$ of the sample would have to consist of a second phase, rich in Ba/Ca and Cu. The XRD pattern is quite clean, and shows no

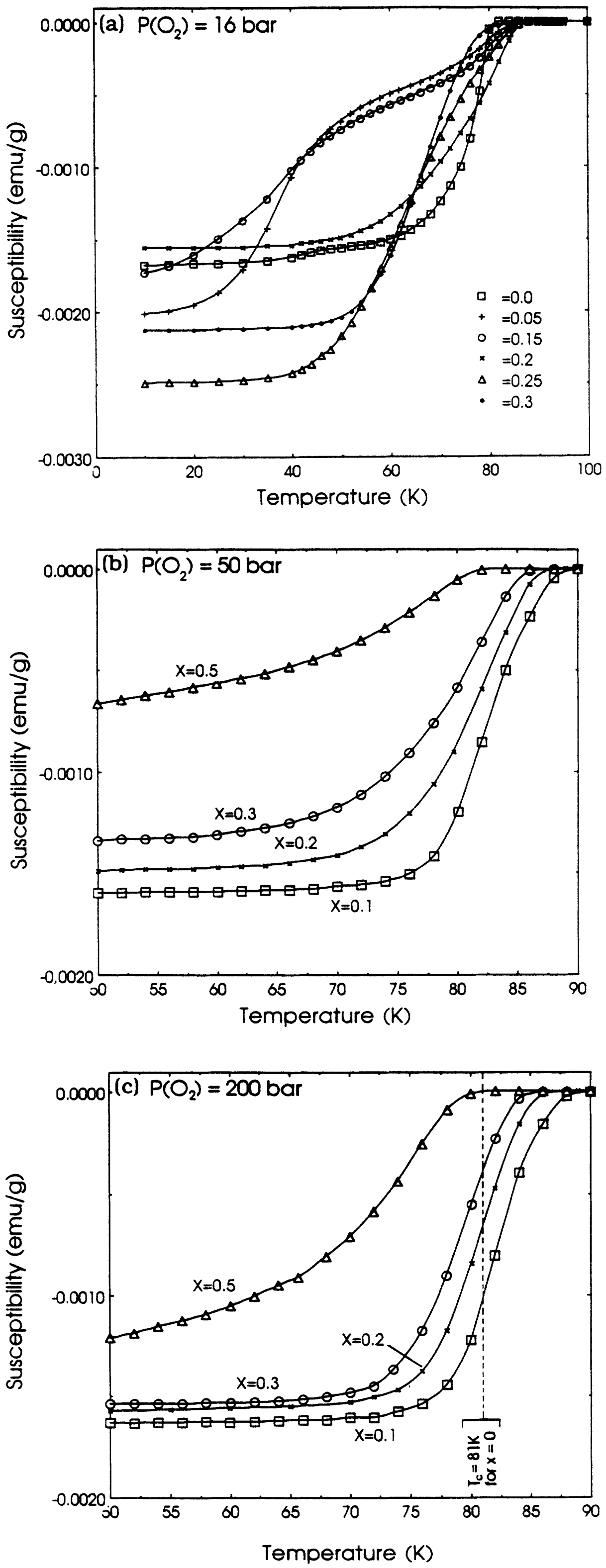

FIG. 3. Diamagnetic susceptibility vs temperature. (a) Calcium substituted tetragonal superconducting 1:2:3 prepared at 16 bars, for six values of x. The highest T_c (86 K) is obtained at $x \approx 0.2$. (b) Calcium substituted 1:2:4 prepared at $P=50$ bars, with four values of x. The T_c of unsubstituted 1:2:4 (81 K) is shown by a dashed vertical line. (c) Calcium substituted 1:2:4 prepared at $P=200$ bars. Ca substitution enhances T_c.

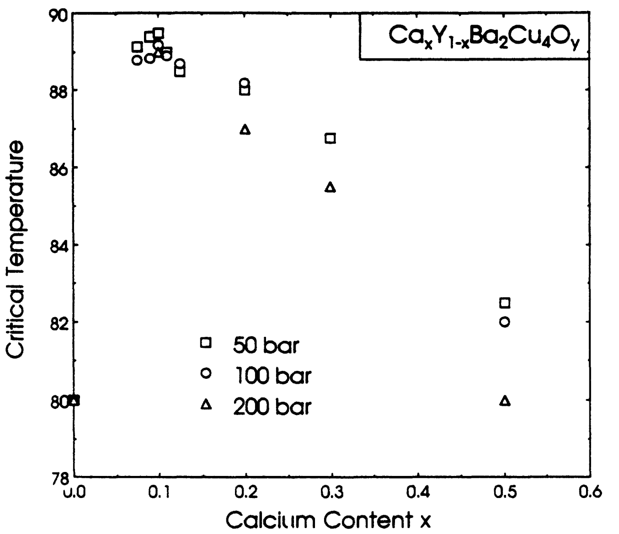

FIG. 4. The variation of T_c (as indicated by the onset of diamagnetism) as a function of x in calcium substituted 1:2:4 ($Ca_xY_{(1-x)}Ba_2Cu_4O_y$) synthesized at 930 °C in $P(O_2)=50$, 100, and 200 bars. Calcium substitution increases T_c from 81 K for $x=0$ up to $T_c=89$ K for $x\approx0.1$. At larger x, and increasing $P(O_2)$, T_c gradually decreases, possibly indicating hole concentration increased beyond the optimum value.

evidence of any such phase, down to the few percent level. We conclude that Ca does in fact replace Y.

B. Ca substituted 1:2:4

Magnetization curves for samples prepared at 50 and 200 bars are shown in Figs. 3(b) and 3(c) (curves at 100 bars are similar). As shown in Fig. 4, T_c reaches a maximum of 89 K at $x=0.1$ and then decreases with larger x. This behavior resembles the T_c versus hole concentration curves presented by Torrance *et al.*[5,8] for 1:2:3 and for $La_{(1-x)}Sr_xCuO_y$. However, it remains to be demonstrated that the average charge per [Cu-O] unit increases with x in $Ca_xY_{(1-x)}Ba_2Cu_4O_y$ and that the resulting holes are mobile. Determination of oxygen content versus x and Hall effect measurement of hole concentration will be needed to confirm Torrance's hypothesis of optimum hole concentration.

Since the enhancement of T_c is obtained at 200_{bars} where the trace second phase is nonsuperconducting, as well as at 50_{bars} where the trace second phase is 1:2:3, it is reasonable to attribute the measured T_c to the majority phase of calcium substituted 1:2:4. However, we note that the magnetization curves showed smooth transitions and no evidence of two T_c's even for those compositions prepared in 50 and 100 bars O_2 which showed evidence of two superconducting phases (1:2:3 and 1:2:4) by XRD. Thus, the smooth demagnetization curves could be misleading. If a small amount of 1:2:3 (below the ~2% detection limit of XRD) is still present, or if a larger amount of 1:2:3 is present as intergrowths with a length scale too small to give sharp XRD lines, 1:2:3 could contribute to the observed T_c enhancement.

CONCLUSIONS

(1) Ca substitution shifts the phase boundaries in the P-T-Composition field to higher $P(O_2)$. The 1:2:3 phase is stabilized at moderately elevated oxygen pressure, and the boundary between 1:2:3 and 1:2:4 moves to higher pressures.

(2) Calcium substitution stabilizes a *tetragonal* 1:2:3 phase with $T_c\approx86$ K at synthesis O_2 pressure ≈16 bars and temperature ≈930 °C. Ca substituted tetragonal 1:2:3 may prove technologically useful because of improved stability as a result of elimination of the tetragonal-orthorhombic transition and associated twinning. The processing conditions are accessible: $P(O_2)\approx16$ bars at 930 °C and possibly considerably lower. Additional studies on this point are in progress.

(3) With increasing Ca substitution, in samples with 1:2:4 majority phase, the transition temperature rises, and then falls with higher Ca. The highest value of T_c is obtained for $[Ca_{0.1}Y_{0.9}]Ba_2Cu_4O_8$.

Note added. While this paper was being prepared, the enhancement of T_c of the 1:2:4 compound synthesized in an oxygen partial pressure of 200 bars with 10% Ca substitution for yttrium was also reported independently by Miyatake *et al.*[9] Their XRD pattern shows a small peak at 38.9° characteristic of 1:2:3, and the unequivocal exclusion of 1:2:3 as a cause of the increased T_c is a problem in their work as well. A search of the literature revealed that Abbattista, *et al.*[10] had reported synthesis of Ba_2CuO_{3+y} with the K_2NiF_4 defect structure prepared at $P(O_2)=1$ bar from the correct starting stoichiometry.

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[1] D. E. Morris *et al.*, Phys. Rev. B **39**, 7347 (1989).

[2] D. E. Morris *et al.*, Physica **159C**, 287 (1989).

[3] D. E. Morris *et al.*, Phys. Rev. B (to be published).

[4] Morris Research, 1862 Euclid Avenue, No. 240, Berkeley, CA 94709.

[5] Y. Tokura *et al.*, Phys. Rev. B **38**, 7156 (1988).

[6] A. Tokiwa *et al.*, Jpn. J. Appl. Phys., **27**, L1009 (1988); M. Kosuge *et al.*, *ibid.* **27**, L1022 (1988); Z. Jirak *et al.*, Physica **156C**, 750 (1988); M. Chandrachood *et al.*, Appl. Phys. Lett. **56**, 183 (1990).

[7] G. Xiao *et al.*, in *High-Temperature Superconductors*, Proceedings of the Materials Research Society Symposium on High-Temperature Superconductors, edited by M. C. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller (Materials Research Society, Pittsburgh, Pennsylvania, 1988), Vol. 99, p. 399.

[8] J. B. Torrance *et al.*, Phys. Rev. Lett. **61**, 1127 (1988).

[9] T. Miyatake *et al.*, Nature **341**, 41 (1989).

[10] F. Abbattista *et al.*, Mater. Res. Bull. **23**, 1509 (1988).