

Role of Ca in enhancing the superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$

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It is known that Ca^{2+} substitution at the Y^{3+} site reduces the superconducting transition temperature (T_c) of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (Y-123) when $y \approx 0$ [Phys. Rev. B **49**, 6385 (1994)]. On the other hand, in the $y \approx 1$ sample, which is nonsuperconducting, 20 at.% Ca at the Y site makes the sample superconducting [J. Solid State Chem. **78**, 192 (1989)]. We have prepared oxygen-deficient samples of the series $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ by annealing them in flowing Ar atmosphere at 400°C. We find that substitution of divalent Ca at the trivalent Y site enhances the superconducting critical temperature T_c of the oxygen-deficient Y-123. From x-ray-diffraction studies, it is observed that the cause of such a contrasting behavior of Ca substitution is the existence of divalent Ca in two different coordination numbers in the discussed system. In the oxygen-deficient Y-123, Ca exists in eightfold coordination while in the fully oxygenated Y-123, it is sixfold coordinated. It is argued that in these compounds the coordination number of Ca is dependent on the oxygen content and the concentration of doped Ca in the material.

I. INTRODUCTION

There are many reports of the studies of Ca substitution at the Y-site in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ system.¹⁻⁸ Several workers^{1-4,8} have found that this decreases the T_c (superconducting transition temperature) of fully oxygenated (pristine sample with $T_c = 90$ K, $y \approx 0$), and the T_c depression in such a situation has been ascribed to the overdoping effect.⁵⁻⁷ In an earlier paper,⁸ some of us argued that in Y-123, Ca exists in a sixfold coordination which necessitates the creation of vacancies in the adjacent Cu-O planes, where superconductivity is primarily supposed to reside, and as a result T_c decreases rapidly. In this paper, by studying the superconductivity in the partially oxygenated $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ system, we further strengthen the previous contention that the role of calcium in suppressing or enhancing the superconductivity of Y-123 is dependent on the existing coordination number of Ca^{2+} in the system. The ionic radii of Ca^{2+} in its sixfold and eightfold coordination are significantly different from each other and thus the observed variation of the c -lattice parameter of the system with Ca doping facilitates one to conjecture the possible coordination number of Ca^{2+} . If Ca^{2+} substitutes at the Y site without disturbing its near-neighbor environment by retaining its eightfold coordination, then it helps superconductivity by increasing the number of holes in the system by enhancing the effective copper valence. On the other hand, if it prefers a sixfold coordination, its nearest-neighbor number decreases which results in the creation of vacancies in the Cu-O planes which is deleterious to T_c .

II. EXPERIMENT

Samples of the series $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ($0 \leq x \leq 0.15$) were prepared by solid-state reaction route

from high-purity Y_2O_3 , CuO, BaCO_3 , and CaCO_3 each of the 4N purity. As prepared samples were further reduced in Ar atmosphere for 12 h at 400°C followed by furnace cooling. ac magnetic susceptibility measurements were carried out on a commercial mutual induction ac setup (Sumitomo) to determine the T_c . The samples were characterized for their phase purity and lattice parameter variations by x-ray diffraction (XRD) using a JEOL diffractometer equipped with Cu $K\alpha$ radiation. The effective Cu valence was determined by the conventional iodometric titration technique.^{9,10} The oxygen content was then calculated considering Y to be in 3+ and Ba in 2+ valence state.

III. RESULTS AND DISCUSSION

In Fig. 1, the room-temperature XRD patterns of the $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ samples are shown. The patterns reveal the single-phase nature of all the samples. The orthorhombic distortion can be well seen, which is less than that observed for fully oxygenated samples.^{8,11} Lattice parameters obtained by a least-squares analysis of the observed d values of all these samples are listed in Table I.

ac susceptibility behavior with temperature in the range of 120–15 K is shown in Fig. 2 for these samples. It is seen that the T_c (defined as the temperature of the onset of diamagnetism) increases with Ca substitution. The rate of increase in T_c with Ca substitution is, however, not monotonic (Table I).

The effective copper valence of the Ca-doped samples increases but the rate of increase is again not monotonic. Calculated oxygen content values and the effective Cu valence are listed in Table I.

The effect of Ca substitution in oxygen deficient (Ar annealed) samples can be summarized as follows:

(1) Up to 15 at. % doping the single-phase material is achieved.

TABLE I. Lattice parameters, a , b , and c , superconducting transition temperature T_c , effective Cu valence, and oxygen content in the system $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$.

Sample	a (Å)	b (Å)	c (Å)	T_c (dia) [K]	Effective Cu valence	Oxygen content
pure	3.8340	3.8699	11.6937	57	2.10	6.65
5 at. % Ca	3.8386	3.8694	11.7328	70	2.15	6.70
10 at. % Ca	3.8320	3.8740	11.7460	75	2.17	6.70
15 at. % Ca	3.8367	3.8670	11.7560	78	2.18	6.71

(2) T_c increases with Ca substitution in oxygen-deficient samples.

(3) The c -lattice parameter increases with Ca substitution.

(4) The effective copper valence of the system increases with Ca substitution.

The above findings reveal that the effect of Ca substitution on oxygen-deficient Y-123 is quite different from that on fully oxygenated samples.^{1-3,8} When the samples are annealed in argon, their oxygen stoichiometry goes down

(Table I). This results in a decrease in the effective copper valence and correspondingly a decrease in the hole concentration in the system (Table I), due to which the T_c of pristine sample is depressed.^{9,11,12} With Ca substitution at the Y site, one is supposed to increase the number of holes and, as a result enhance the superconductivity. The above situation is feasible only if the coordination number of Ca remains the same as that of Y. In contrast to our findings in fully oxygenated samples,⁸ the present study on oxygen-deficient samples reveals that the c -lattice parameter increases (Table I) with Ca doping. This indicates that Ca enters at the Y site with an ionic radius higher than that of Y. The ionic size of Y in eightfold coordination (existing coordination number in Y-123) is 1.02 Å, while that of Ca in sixfold coordination is 1.0 Å and in eightfold coordination is 1.12 Å. Thus in the present case, the increase in the c -lattice parameter with Ca doping may indeed be attributed to the possible preference of Ca for eightfold coordination in the system. In such a situation, the Ca substitution increases the number of holes in the system and as a result it enhances T_c . In the present case the T_c first increases sharply and later the effect is reduced. At the same time c parameter also increases at a faster rate in the initial stage and subsequently at a much slower rate. This reflects that for $x < 0.05$, Ca prefers only eightfold coordination, while with further increase in x (> 0.05), it seems to have both sixfold and eightfold coordinations. The former situation is clearly more favorable for superconductivity.

In summary, we have studied the effect of calcium on

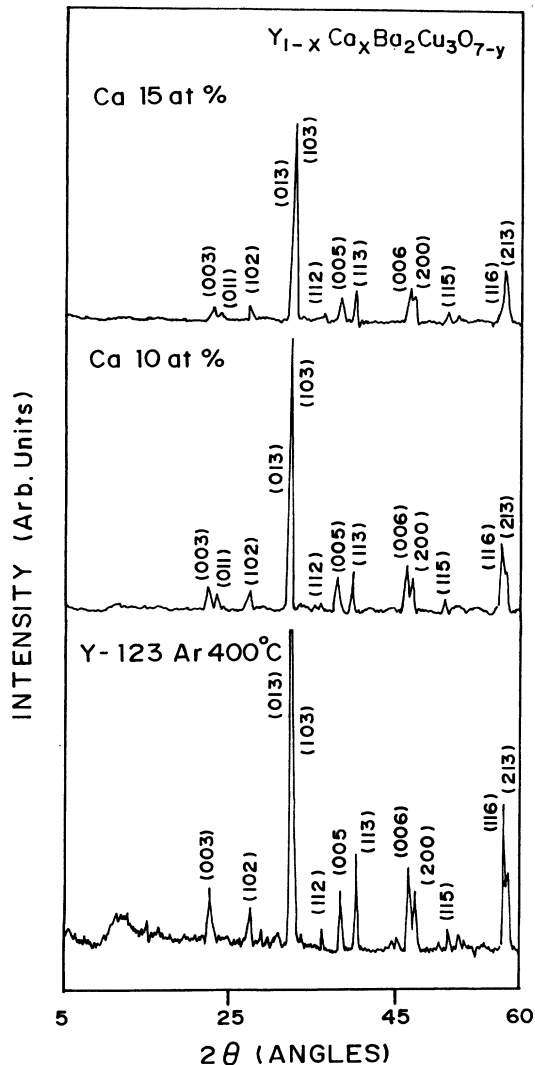


FIG. 1. XRD patterns taken at room temperature for the $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ system with $0.0 \leq x \leq 0.15$.

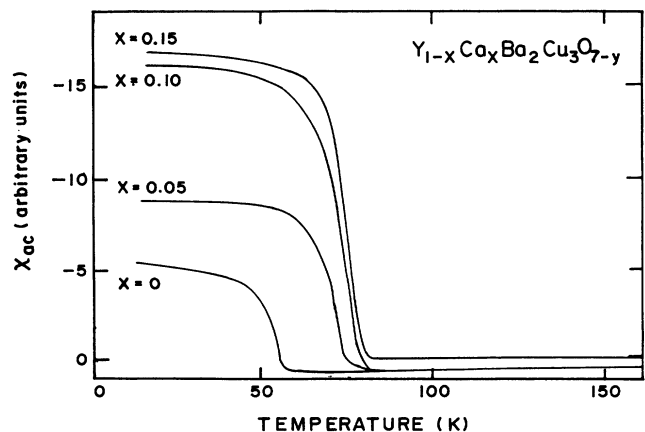


FIG. 2. AC susceptibility behavior with temperature for the $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ system with $0.0 \leq x \leq 0.15$.

the superconductivity of Y-123. An explanation is provided for enhancement or suppression of superconductivity of Y-123 with Ca doping which involves the coordination number or the near-neighbor environment of the Ca in the doped system. It is found that eightfold coordi-

nated Ca at the Y site enhances the superconductivity, while with sixfold coordination it has deleterious effect. It would be interesting to carry out neutron-diffraction studies on each samples to ascertain the near-neighbor oxygen environment of Ca.

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