

Role of calcium in suppressing the superconductivity of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$

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Partial substitution of Ca^{2+} at the Y^{3+} site in the $YBa_2Cu_3O_{7-\delta}$ system shows several interesting features, namely (1) creation of oxygen vacancies without any change in the lattice parameters, (2) no change in the effective copper valence, and (3) decrease in the critical temperature T_c with substitution, accompanied by a decrease in the normal-state conductivity. A host of measurements such as low-temperature resistivity, magnetic susceptibility, x-ray diffraction, oxygen stoichiometry, and the effective copper valence, reported here, suggest that T_c depression with Ca substitution is unlikely to be due to an overdoping effect. An alternate explanation, which takes stock of the above observations, and involves the creation of disorder in CuO_2 planes, is invoked.

I. INTRODUCTION

The aliovalent substitutions in high- T_c superconductors are of considerable interest, as they can substantially change the effective copper valence in the cuprate superconductors.^{1,2} The copper valence is intimately linked with the carrier concentration n , and by studying T_c as a function of n , detailed phase diagrams have been determined for the Sr- (or Ba-) doped La 2:1:4 system.^{3,4} The beauty of such a phase diagram is that the T_c of the material decreases both before and after an optimum carrier concentration.^{3,4} Attempts have been made to generalize such behavior to various other families of high- T_c cuprates, namely R 1:2:3 as well as Bi- and Tl-based systems.⁵ It has been argued that, unlike La 2:1:4, the situation with other cuprates is not so transparent, as the data available are either too scant or not sufficiently unambiguous because of the simultaneous presence of two fluctuating-valence cations⁶ such as Cu and Bi (or Tl). As with the La 2:1:4 system, T_c behavior in the underdoped regime in the 1:2:3 system is well established, but the overdoped regime is yet to be properly explored. It is well understood that in R 1:2:3 the carrier density can be enhanced either by increasing the oxygen stoichiometry or by on-site cationic substitutions with dopants of lower valence state. By increasing the oxygen stoichiometry, the copper valence in general cannot be increased beyond its optimum value, due to structural instability. In such a situation the only alternate strategy left is to realize the objective by substitution of lower-valence-state cations.

In the case of the R 1:2:3 system, one of the most extensively studied substitutions is where R^{3+} is partly replaced by Ca^{2+} .⁷⁻¹² The results reported in the literature are however varied, which reveals that such a substitution creates vacancies.^{9,12} Interestingly at the same time the x-ray-diffraction (XRD) data of other workers indicate literally no change in the lattice parameters of the parent material up to 20 at. % of Ca substitution.^{9,10} This remarkable behavior remains to be understood. This apart, the T_c decrease with Ca substitution has been attributed to the material becoming overdoped.^{9,12} Such

a contention also calls for a further examination.

In this paper we present systematic data of measurements made on Ca^{2+} -doped (at the Y^{3+} site) Y 1:2:3 samples. Resistivity, XRD, susceptibility, effective copper valence, and oxygen stoichiometry are measured to gain insight into the above issues.

EXPERIMENT

Samples of a Ca-substituted Y 1:2:3 series were prepared from high-purity Y and Cu oxides, and Ba and Ca carbonates, each of 4N purity, by the solid-state reaction route as followed for the synthesis of this system. Four-probe dc resistivity data of rectangular slab samples were obtained in the temperature range of 70 to 300 K, in a liquid-nitrogen-bath cryostat, using a platinum resistance thermometer sensor. The entire measurement system, consisting of a nanovoltmeter (Keithley 181), a constant-current source (Keithley 224), a temperature controller, and an indicator (Lakeshore model 820), was hooked to a HP 216 system controller for automatic data acquisition and control. Magnetic-susceptibility measurements were carried out with a computer-controlled ac susceptometer (Lakeshore 7000). The samples were characterized for phase identification, homogeneity, and lattice parameters by XRD using a Siemens D-500 diffractometer with Cu $K\alpha$ radiation. The effective copper valence was estimated by the conventional iodometric titration technique.^{13,14} The oxygen content was then determined taking Y to be in the 3+ and Ba and Ca to be in 2+ valence state.

RESULTS

Figure 1(a) depicts the resistivity-versus-temperature behavior of the Ca^{2+} -doped Y 1:2:3 system. The critical temperature [$T_c(R=0)$] of the system decreases monotonically with Ca^{2+} incorporation in place of Y^{3+} . The normal-state conductivity of the system also decreases with substitution. Quantitative data of all these samples pertaining to the resistivity measurements are given in Table I. Values of $T_c(R=0)$, T_c (onset),

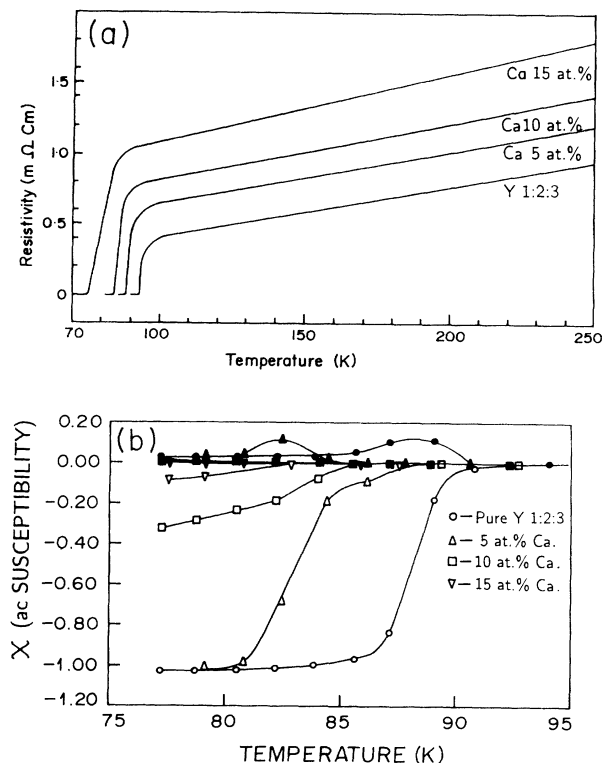


FIG. 1. (a) Resistivity versus temperature of the Ca-doped Y 1:2:3 system. (b) ac susceptibility (χ) versus temperature of the Ca-doped Y 1:2:3 system.

normal-state resistivity at 250 K, and also at just above T_c are listed.

The ac susceptibility behavior with temperature for the above samples is given in Fig. 1(b). Susceptibility data corroborate well with the $T_c(R=0)$ values. The concentration-dependent $T_c(\chi)$ values given in Table I correspond to the temperatures where the ac susceptibility becomes diamagnetic.

Figure 2 shows the room-temperature XRD patterns of Ca-doped Y 1:2:3 samples, with increasing Ca concentration. As can be seen from Fig. 2, the orthorhombic splittings, indicated by (110), (103), with (020), (200) and (123), (213), are quite similar in both pure and Ca-doped Y 1:2:3, indicating no obvious change in the orthorhombicity of the system. Lattice parameters a , b , and c are listed in Table I. It is evident that there is no significant change in a , b , and c parameters with Ca incorporation, which is in agreement with the earlier reports.^{10,12}

The effective copper valence of the system as measured

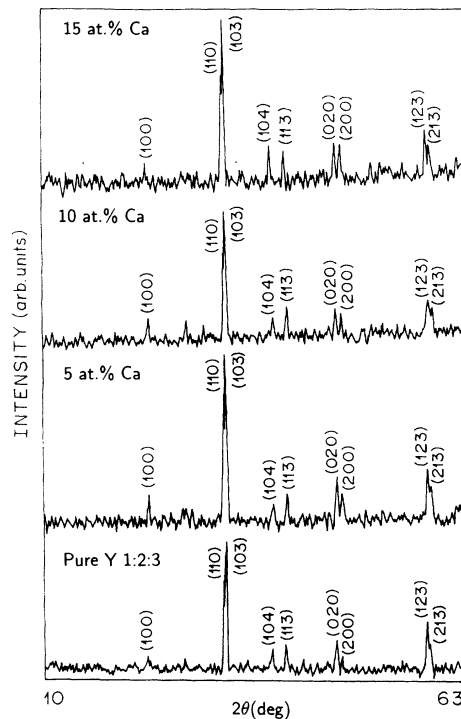


FIG. 2. XRD patterns shown one above the other for the Ca-doped Y 1:2:3 system. Calcium content increases from bottom to top.

through iodometry is also listed in Table I. The table gives the calculated value of the oxygen content. As may be seen, the effective copper valence does not change much with incorporation of Ca, which is in general accord with other work,^{9,12} while the oxygen content of the system decreases when Ca^{2+} is substituted for Y^{3+} . Decrease in the oxygen content leading to oxygen vacancies also agrees with previous thermogravimetric-analysis reports.^{9,10,12}

DISCUSSION

Clearly Ca^{2+} incorporation within the solubility limits in place of Y^{3+} has three main effects: (1) Decrease of $T_c(R=0)$, T_c (onset), and normal-state conductivity, (2) Lattice parameters a , b , and c remain invariant, and (3) Effective copper valence essentially remains unchanged while the oxygen stoichiometry of the system is decreased.

The invariance (in fact a small decrease) of Cu valence with Ca doping is contrary to the general belief that Ca substitution leads to overdoping^{9,12} of the 1:2:3 system,

TABLE I. Quantitative data for the Ca-doped Y 1:2:3 system.

| Sample | $\rho(250 \text{ K})$ $\Omega^{-1} \text{ cm}$ | ρ (onset) $(\Omega^{-1} \text{ cm})$ | T_c (K) | T_c (onset) (K) | $T_c(\chi)$ (K) | a (Å) | b (Å) | c (Å) | Oxygen content | Effective Cu valence |
|---------|---|--|--------------|----------------------|--------------------|------------|------------|------------|----------------|----------------------|
| Y 1:2:3 | 0.90 | 0.40 | 93 | 94.5 | 92 | 3.82 | 3.88 | 11.68 | 6.93 | 2.31 |
| 5% Ca | 1.15 | 0.60 | 88 | 88 | 89 | 2.82 | 3.87 | 11.67 | 6.82 | 2.29 |
| 10% Ca | 1.50 | 0.80 | 84 | 87 | 84 | 3.81 | 3.87 | 11.67 | 6.80 | 2.30 |
| 15% Ca | 1.70 | 1.00 | 75 | 81 | 77 | 3.81 | 3.86 | 11.66 | 6.69 | 2.28 |

and thereby lowers T_c . The contention of overdoping is further contradicted by the decrease in the normal-state conductivity of Ca-doped samples. Likewise the suggestion that pure stoichiometric Y 1:2:3 is overdoped¹¹ is not substantiated by these observations. Consequently, the explanation of the observed T_c decrease due to Ca incorporation is possibly different.

There is no change found in a , b , and c lattice parameters while the oxygen stoichiometry of the system is increased. In a pure R 1:2:3, decrease in oxygen stoichiometry creates vacancies in Cu-O chains, resulting in a decrease in orthorhombicity.¹ In the present case, as there is no change found in the orthorhombicity of the system, the oxygen is presumably not removed from the Cu-O chains. Interestingly, there is no change noted in the c parameter with Ca incorporation. This suggests that Ca enters at the Y site with the same ionic radius as Y. The ionic size of Y^{3+} in eightfold coordination is 1.02 Å, which matches more closely with that of Ca^{2+} in sixfold coordination (1.0 Å) than in eightfold coordination (1.12 Å). This suggests that Ca at a Y site would prefer

sixfold instead of eightfold coordination. This would necessarily imply creation of oxygen vacancies in the adjoining CuO_2 planes. Since superconductivity is presumably supposed to reside in these planes, the oxygen disorder thus created is expected to have deleterious effect on T_c , which is observed with Ca substitution. However, this effect would also explain the decrease in the conductivity of the doped samples. The above explanation we believe is unique in indicating the role of Ca substitution in the superconductivity of Y 1:2:3, taking account of all the observations, namely, creation of vacancies without any change in lattice parameters, invariance of copper valence, and decrease in T_c with Ca substitution.

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