Possible Superconductivity and Microstructural Investigation in Y$_{1-x}$Ca$_x$SrCu$_{2.6}$Fe$_{0.4}$O$_{6+z}$ (x = 0, 0.1)

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Preparation, X-ray diffraction, electron diffraction and microscopy, and energy dispersive X-ray analyses of Y$_{1-x}$Ca$_x$SrCu$_{2.6}$Fe$_{0.4}$O$_{6+z}$ (x = 0, 0.1) are described. Zero resistivity was observed at 10 K for x = 0, which increased to 25 K for x = 0.1. These were confirmed by AC susceptibility measurements. Possible observation of superconductivity in this system is discussed. © 1991 Academic Press, Inc.

Introduction

The effect of substitution on structural and superconducting properties has been extensively studied in the case of YBa$_2$Cu$_3$O$_{6+z}$ (1). Whereas there is a fair agreement among different reports on the results obtained in substitutional studies at the Y and at the Cu site, controversial results have been reported on the substitution of Ba by Sr in YBa$_{2-k}$Sr$_k$Cu$_3$O$_{6+z}$. While some have observed that for k > 1, the perovskite structure was not stable (2), others have observed superconductivity at T_c (resistivity ρ = 0) ranging between 72 and 90 K in Y–Sr–Cu–O, depending on the preparation conditions (3). Recently, Sunshine et al. (4) have studied in detail the effect of 3d metal doping at the Cu

site on the structural and superconducting properties of YSr$_2$Cu$_{3-y}$M$_y$O$_{6+z}$ (M = Fe, Co, Al). In particular, they have observed that the perovskite structure can be stabilized for y > 0.3, and superconductivity was indeed observed at T_c = 10 K for M = Fe (y = 0.30) but not for M = Al. In view of the fact that the superconducting volume fraction was less than 2%, they could not attribute it uniquely to the perovskite phase. In spite of this uncertainty, we thought it was worthwhile reexamining this system. Furthermore, we wanted to investigate if the hole concentration in the above system could be modified by an additional substitution of Y by Ca. We report here on the preparation, electrical and magnetic properties, X-ray diffraction (XRD), electron diffraction (ED) and mi-

croscopy, and energy dispersive X-ray (EDX) analyses of $Y_{1-x}Ca_xSr_2Cu_{2.6}Fe_{0.4}O_{6+z}$ ($x = 0, 0.1$).

Experimental Techniques

The polycrystalline samples have been prepared by solid state sintering of the respective oxides or carbonates. The chemicals were of 99.999% purity. Y_2O_3, $SrCO_3$, $BaCO_3$, CuO, and Fe_2O_3 were thoroughly mixed in required proportions and calcined at 950°C in air for a period of 12–18 hr. The resulting product was ground, mixed, pelletized, and heated in air at 980°C for a period of 16–24 hr. This was repeated once. The samples were finally annealed in oxygen at 500°C for a period of 60–72 hr and furnace cooled. These are denoted as $1 ($x = 0$) and $2 ($x = 0.1$). Between 15 and 25 X-ray ($CuK\alpha$) reflections were used to fit the pattern and to calculate the lattice parameters. Electron diffraction and microscopy were carried out on small platelets crushed in an agate mortar. Quantitative analyses of some of the samples by EDX technique were carried out in a Philips 505, 15 kV scanning microscope provided with an EDX Link Analytical AN 10000 spectrometer (5). Indium was ultrasonically soldered at four points of the pellets, and the resistivity was obtained by AC technique. Superconducting transitions were also checked by measuring both the real (χ') and the imaginary (χ'') parts of the AC susceptibility in a field of 0.2 Oe and at a frequency of 1500 Hz.

Results and Discussion

XRD analyses of the samples revealed a few impurity reflections whose intensities were less than 5%. The lattice parameters of the sample $1 were found to be $a = b = 3.808$ Å and $c = 11.397$ Å, which agree very well with those reported by Sunshine *et al.*(4). The RMS deviation of 2θ was $8 \times$

FIG. 1. Electron micrograph of a large piece of crystal ($1) of $YSr_2(CuFe)_3O_{6+z}$ showing either a dislocation or a sub-grain boundary ($\times 42,500$).

10^{-2}. The lattice parameters of $2 were found to be $a = 3.802$, $b = 3.804$, and $c = 11.410$ Å. The small difference in a and b could be due to experimental errors. The small increase in the c parameter could be due to the substitution of Ca at the Y site as was also observed, for example, by Manthiram *et al.* (6) in the case of $Y_{1-x}Ca_x Ba_2Cu_3O_{6+z}$.

The electron micrograph of $1 (Fig. 1) reveals very few defects, and there are no indications of any twins, indicating the absence of orthorhombic distortion. The corresponding electron diffraction pattern (EDP) shown in Fig. 2 further confirms the tetragonal symmetry. The lattice parameters calculated from this pattern ($a = b = 3.82$ Å and $c = 11.45$ Å) agree fairly well with those derived from the XRD pattern. More than 75% of the matrix of the analyzed crystals contain a single phase and they have all possible orientations. One such orientation is shown in Fig. 2. Less than 5% of the matrix contains other phases such as $YCuO_2$, $Y_2Cu_2O_5$, $SrCu_{1.65}O_{2.65}$, and $Y_2Sr CuO_5$. In particular, Y_2SrCuO_5 was identified, whose lattice parameters were found (7) to be $a = 7.1$, $b = 12.06$, and $c = 11.16$
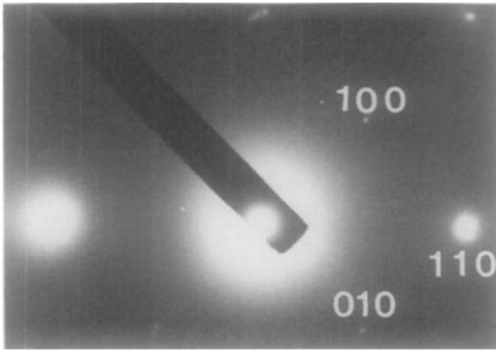
FIG. 2. EDP (zone axis [0 0 1]) corresponding to $1 showing clearly the tetragonal structure.

Å. Similar results were obtained in the case of $2. The EDP of $2 showed that the majority of the sample consists of a tetragonal phase with $a = b = 3.82$ Å and $c = 11.45$ Å. In general, the crystals of $2 are disoriented and smaller than those of $1. No twin structures were seen.

The EDX technique was used to analyze the composition on the surface (130 × 130 μm^2) and in volume (2.5 μm^3) of the samples 1 and 2. About 150 points were examined. The results are summarized in Table I. In general a high degree of homogeneity in composition on the surface was observed. The average surface composition of $1 is found to be $Y_{1.1}Sr_{2.1}Cu_{2.6}Fe_{0.45}O_t$ (6.9 < t < 7.1). About 70% of $1 had this composition in volume; about 15% had varying contents of Y, Sr, Cu, and Fe. Similar comments apply to $2, which contained 78% of $Y_{1.05}Ca_{0.1}Sr_{2.05}Cu_{2.65}Fe_{0.45}O_t$. A uniform distribution of Ca was observed.

The resistivity (ρ) as a function of temperature of $1 and $2 is shown in Fig. 3a. ρ of $1 at 300 K is around 2.5 mΩ cm, which is about 4 times smaller than that reported (4). It decreases slowly with T down to 150 K and then increases slowly. At around 20 K, it starts decreasing, and zero resistivity is observed at $T_c = 10$ K. No such transition is reported in Ref. (4) for a similar composition. Remarkable changes appear in ρ and

T_c in the case of $2 ($x = 0.1$). ρ at 300 K is around 1.5 mΩ cm and decreases steadily with T. A very small increase is seen at 55 K before it decreases to zero at $T_c = 25$ K, the increase in T_c being 15 K compared to that of $1 and to that reported in Ref. (4) in the case of $YSr_2Cu_{2.7}Fe_{0.3}O_7$. These findings are further confirmed by AC susceptibility data, discussed below.

The real (χ') and the imaginary (χ'') parts of the AC susceptibility as a function of temperature of the above samples are shown in Fig. 3b. All the samples used for the measurements had the same shape and size. This allows us to compare the amplitude of
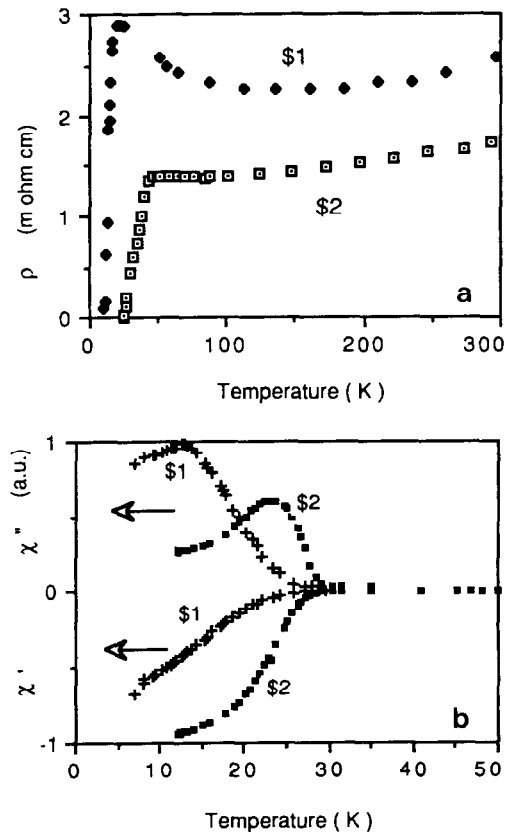

FIG. 3. (a) Resistivity as a function of temperature of $Y_{1-x}Ca_xSrCu_{2.6}Fe_{0.4}O_{6+z}$ ($1, x = 0$; $2, x = 0.1$). (b) Real (χ') and imaginary (χ'') parts of the AC susceptibility as a function of temperature of $1 and $2.

TABLE I

EDX ANALYSES OF $Y_{1-y}Ca_ySr_2Cu_{2.6}Fe_{0.4}O_{6+z}$

Y	Ca	Sr	Cu	Fe	% present
			Sample $1		
1.05	0	2.1	2.65	0.45	72
1.0	0	2.0	2.8	0.5	9
1.1	0	2.2	2.45	0.45	4
0.45 to 1.6	0	0.9 to 3	1.15 to 4.3	0.25 to 0.7	15
			Sample $2		
1.05	0.1	2.05	2.65	0.45	78
0.95	0.1	1.95	2.8	0.45	8
1.1	0.1	2.15	2.4	0.4	4
		other compositions: $CuO,(Ysr)CuO_t$, $SrCuO_2$			10

Note. $1 - y = 0$; $2 - y = 0.1$.

the signals of each sample, though the units used are arbitrary. A broad diamagnetic transition starting at $T_d = 22$ K is observed in the case of $1. Starting from 5 K, the field penetrates the sample, indicating superconductivity between weakly connected grains. The corresponding χ'' peak located at 14 K is also very broad. However, in the case of $2 with $x = 0.1$ Ca, the diamagnetic onset occurs at a higher temperature, $T_d = 28$ K, with an increase in amplitude of the signal, and the width of the transition (90%–10%) is around 13 K. The field penetration starts only for $T > 10$ K, indicating a better connectivity between the grains compared to $1. The corresponding χ'' peak is also located at a higher temperature, at around 22 K, compared to that of $1 and further has a smaller width of around 10 K.

We would like to make the following comments concerning the occurrence of superconductivity in our samples. Let us note that Sunshine *et al.* (4) have observed a very large resistive transition with $T_c = 10$ K in $YSr_2Cu_{2.7}Fe_{0.3}O_{6+z}$ and a small diamagnetic DC susceptibility in a SQUID magnetometer for the Fe 0.35 sample from which they estimate only a 2% superconducting frac-

tion. Neither the field under which it was measured nor the method—whether the sample was field cooled or zero field cooled—was explicitly mentioned. We have measured the superconducting screening effect by the AC susceptibility technique, where an alternating field (1500 Hz) of 0.22 Oe was used. The maximum signal observed in the case of $1 corresponds to about 22% of that observed in the case of a well characterized $YBa_2Cu_3O_{6.95}$, of similar shape and size, and in the case of $2 it corresponds to about 35%. Furthermore, the impurities observed in the EDX analyses of both these samples correspond to well established insulators. Hence, we find it difficult to attribute the observed diamagnetic transition to these insulating impurity phases. The fact that the width of the transitions (both χ' and χ'') reduce on the addition of Ca indicates that the superconducting grains increase in number and become well connected, probably because of a change in hole density induced by Ca substitution. There is perhaps still scope for reducing the widths of the transitions if one can optimize the annealing conditions.

It is well accepted that the Ca^{2+} ion has a

stronger preference for eightfold coordination, and for smaller concentrations, as in the present case, could replace Y^{3+} (6, 8). It is quite conceivable that Fe^{3+} going to the Cu chain site deprives it of the oxygen in the Cu–O(2) planes, which can be compensated to some extent by Ca doping. It is interesting to note that in the case of the insulating $YBa_2Cu_3O_6$ it was pointed out that the superconductivity could be restored by reducing the electron count by a proper replacement of Y, though Ca was not explicitly suggested (9). Such a substitution would result in the lowering of the Fermi level, and the system would tend to move away from an SDW instability (9). Modification of the oxidation state of the Cu–O layer by Ca was also earlier pointed out (6). Indeed, our preliminary Hall data indicate that the hole density increases from 4.5 to $4.9 \times 10^{21}/cm^3$ as 0.1 Ca is added. It is interesting to point out here that in $Y_{1-x}Ca_xSrBaCu_{2.8}Al_{0.2}O_{6+z}$ as x was increased from 0 to 0.2, the T_c increased by about 25 K, resulting in narrower transitions, and this was accompanied by an increase in the hole density (10). Further studies, such as the effect of oxygen annealing as a function of Fe and Ca concentrations, are in progress, which should confirm these preliminary results.

In conclusion, we have reported on the preparation, XRD, electron diffraction and microscopy, and EDX analyses of $Y_{1-x}Ca_x$ $Sr_2Cu_{2.6}Fe_{0.4}O_{6+z}$ ($x = 0, 0.1$). For $x = 0$, zero resistivity was observed at 10 K, which increased to 25 K for $x = 0.1$. These were confirmed by AC susceptibility measurements. The fact that this perovskite-type compound with 13% of Fe does not contain Ba and still shows superconductivity should warrant further investigations, and this makes it an interesting system for studies on the structural origin of holes and the role played by crystal chemistry on the mecha-

nism of high temperature superconductivity.

Acknowledgments

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