Hole Doping and Oxygen-Pressure Stability Studies in the Layered Cuprate $Ca_{0.85}Sr_{0.15}CuO_2$

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The possibility of hole doping in $Ca_{0.85}Sr_{0.15}CuO_2$ was studied by either partial substitution of alkaline-earth cations by Li and Na or by annealing in oxygen pressures up to 200 atm. Li substitution does not modify significantly the cell parameters, but results in changes in X-ray reflection intensities and increases in electrical conductivity. Sodium does not substitute in the $Ca_{0.85}Sr_{0.15}CuO_2$ phase. Oxygen-pressure treatments up to 975°C and 200 atm O_2 show a reversible transformation between layered $Ca_{0.85}Sr_{0.15}CuO_2$ and the chain-containing $Ca_6Cu_7O_{14}$, which is more stable at high oxygen pressure. © 1994 Academic Press, Inc.

INTRODUCTION

The bidimensional character of superconducting cuprates has been a constant feature since the discovery of high-temperature superconductivity in 1986. The "ultimate" structural example of bidimensional copper oxide is $Ca_{1-x}Sr_xCuO_2$, which consists of alternating infinite layers of Ca(Sr) and CuO_2 planes (1), a structure type which will be referred to as "$Cu\infty$" throughout this text. $Ca_{1-x}Sr_xCuO_2$ prepared at ambient pressure has a very limited range of alkaline-earth solid solution x around 0.12 (2) and is not a superconductor.

In 1989, Takano *et al.* (3) showed that the $Cu\infty$ structure can be stabilized for a wide range of alkaline-earth compositions under high pressure. Superconductivity in these high-pressure phases was reported both in the Sr–Ca–Cu–O system (4) and, with higher superconducting volume fractions, in rare-earth-doped $Sr_{1-x}Ln_xCuO_2$ (5). The latter case clearly corresponds to electron doping. Hole doping is considerably more difficult to achieve; it requires alkaline-earth-deficient compositions and oxidizing atmospheres usually supplied by adding potassium perchlorate to the reaction medium under high pressure (6, 7). Meissner volume fractions in excess of 20% in the Sr–Ca–Cu–O system were achieved only recently (8). The samples obtained are not single-phase, and more work is needed to ascertain the nature of the actual superconducting phase in high-pressure Ca–Sr–Cu–O oxides (9).

Returning to ambient pressure chemistry, which is not hampered by the problems of sample volume and bad reproducibility often inherent to high-pressure synthesis, one question remains: can $Ca_{0.85}Sr_{0.15}CuO_2$ be hole-doped, or, in other terms, can the formal valence of copper be increased in this compound?

Superconducting hole-doped cuprates can be obtained from Cu^{2+} stoichiometric parent compounds either by partial substitution with aliovalent cations of lower charge or by doping with excess oxygen atoms. These two routes, which both result in increasing the formal valence of copper, are well documented for lanthanum cuprate La_2CuO_4.

Attempts to substitute alkali-metal cations in $Ca_{0.85}Sr_{0.15}CuO_2$ were briefly described by Matsuo *et al.* (10), who concluded that it is "very hard to achieve hole doping" by Li or Na substitution under ambient pressure. Significant changes in the electrical conductivity and in the magnetic susceptibility as a function of lithium doping were reported by Brinda *et al.* (11). Superconductivity was not achieved, however.

The effect of oxygen pressure on bulk samples has not been investigated previously to our knowledge. On thin films, Kobayashi *et al.* (12) noted an increase in conductivity by two orders of magnitude after postannealing in 1 atm oxygen, whereas Li *et al.* (13) observed resistive and magnetic anomalies after atomic deposition of $Ca_{1-x}Sr_xCuO_2$ in a NO_2 atmosphere.

The purpose of the present work is to investigate hole doping in $Ca_{0.85}Sr_{0.15}CuO_2$ by either alkali cation substitution or annealing under oxygen pressures up to 20 MPa. The latter technique yielded an unexpected result: a reversible phase transition toward $Ca_6Cu_7O_{14}$, a nonsuperconducting. NaCuO$_2$-type compound, as a function of oxygen pressure.

EXPERIMENTAL

Starting materials were 99.9% $CaCO_3$, $SrCO_3$, and CuO. Calcium and strontium carbonates were calcined at 1200°C to yield the oxides. Alkali metals were supplied as

TABLE 1

Ionic Radii of Relevant Cations, in Å (Based on $r(O^{2-}) = 1.40$ Å) (15)

Cation	Square planar coordinate	Coordinate 8	Observed in $Ca_{0.85}Sr_{0.15}CuO_2$ (1)
Cu^{2+}	0.57	—	0.531
$(Ca_{0.85}Sr_{0.15})$	—	1.14	1.107
Li^+	0.76^a	0.92	
Na^+	1.02^a	1.18	

^{a} Square planar coordinate rare; data for octahedral coordinate.

TABLE 2

Cell Parameters of Alkali-Substituted $A_y(Ca_{0.85}Sr_{0.15})_{1-y}CuO_z$ (in Å)

A	y	a	c
—	—	3.864(1)	3.219(1)
Li	0.10	3.866(1)	3.219(1)
	0.15	3.864(2)	3.218(1)
	0.20	3.858(1)	3.214(1)
Na	0.15	3.864(2)	3.212(3)
	0.25	3.863(2)	3.211(1)

lithium carbonate or sodium peroxide. The oxide mixtures were ball milled, pelletized, and fired repeatedly at 950–1000°C in air for periods of 24 hr in gold crucibles, with intermediate regrinding.

As noted in previous studies (14), numerous firings are necessary to obtain the Cu∞ phase at ambient pressure. X-ray diffraction showed that the emergence of $Ca_{0.85}Sr_{0.15}CuO_2$ requires at least five heat treatments/regrinding cycles. Single-phase $Ca_{0.85}Sr_{0.15}CuO_2$ was not obtained before the ninth treatment, i.e., more than 300 hr total heating.

Annealings under oxygen pressure were carried out on powders enclosed in gold tubes placed in stainless steel autoclaves operating up to 900°C and 20 MPa oxygen pressure.

Samples were characterized by powder X-ray diffraction using a Guinier focusing camera with $FeK\alpha$ radiation and internal silicon standard. Cell parameters and theoretical intensities were calculated using the Celref and Lazy Puverix computer programs, respectively. Sodium contents were determined by absorption atomic spectrophotometry after dissolution of samples in hydrochloric acid. Superconductivity was tested by ac susceptibility measurements, using a mutual inductance bridge.

RESULTS AND DISCUSSION

Alkali-Metal Doping

A comparison of ionic radii (see Table 1) shows that suitable monovalent cations for doping in $Ca_{0.85}Sr_{0.15}CuO_2$ are Li^+ and Na^+. In the case of lithium, the dopant size is intermediate between that of Cu^{2+} and the alkaline earths, so that the host site cannot be simply inferred from ionic radius considerations.

Lithium. The synthesis of samples of nominal composition $Li_y(Ca_{0.85}Sr_{0.15})_{1-y}CuO_z$ ($y \leq 0.20$) was carried out at 930°C until the X-ray patterns were unchanged. Unlike undoped $Ca_{0.85}Sr_{0.15}CuO_2$, only multiphase samples were obtained, even after additional heat treatments. The main

secondary phases were CuO and $(Ca_{1-x}Sr_x)_2CuO_3$. In addition, the measured cell parameters of the Cu∞ phase were independent of y within experimental errors (see Table 2). We also carried out relative measurements of the electrical conductivity on sintered pellets, resulting in a significant increase in conductivity with the nominal lithium content. The resistivities were on the order of 0.1 to 1 Ω cm at room temperature, and they showed a semiconducting behavior.

These data are in agreement with those of Brinda *et al.* (11). More convincing results have been reported recently on thin films of composition $Ca_{1-y}Li_yCuO_2$ (16). These films show a semiconducting behavior at all y values up to 0.4, and the conductivity increases with the lithium content. The cell parameter variation is very small. Kubo *et al.* (16) also noted that the evolution of 001 reflection intensities correlates with the lithium content in the case of substitution on the calcium site. The calculated intensity ratios 001/002 are plotted in Fig. I for both copper
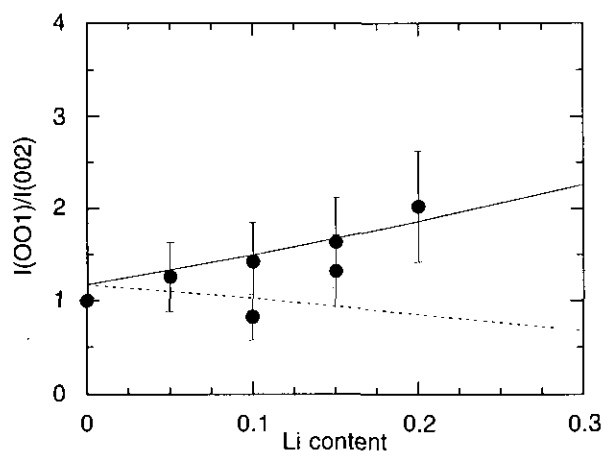

FIG. 1. Evolution of the intensity ratio of reflections 001 and 002 in $Li_y(Ca_{0.85}Sr_{0.15})_{1-y}CuO_z$ as a function of Li content. Full line, calculated for Li on the Ca site; dashed line, calculated for Li on the Cu site; ●, experimental points.

and calcium substitution. Our experimental results show a rather good agreement with the latter case (Fig. 1). In fact, this change in X-ray reflection intensities is the most convincing evidence of lithium doping in the $Cu\infty$ structure so far.

None of these lithium-doped samples showed any metallic or superconducting behavior.

Sodium. Syntheses with starting compositions $Na_y(Ca_{0.85}Sr_{0.15})_{1-y}CuO_z$ ($y \leq 0.25$) gave the following results: (i) traces of CuO in the X-ray patterns for $0.15 \leq y \leq 0.25$, (ii) no changes in cell parameters as a function of y (see Table 2), and (iii) partial melting at 980°C, resulting in some gold crucible corrosion, (iv) significant mass losses on annealing up to the third heat treatment at 950°C.

In addition, the determination of the sodium contents yielded in all cases y values lower than 0.002, i.e., two orders of magnitude smaller than nominal compositions. ac susceptibility tests showed the absence of any diamagnetic signal down to 4 K.

These results indicate that the solubility of sodium in the $Ca_{0.85}Sr_{0.15}CuO_2$ phase is very limited. Most of the sodium oxide, which is known to be volatile above ca. 900°C, is lost during the heat treatments. No cation-deficient phase seems to be formed either, as shown by the presence of remaining copper oxide in the X-ray diffraction spectra. The reaction can be summarized as follows:

$$\text{"}Na_y(Ca_{0.85}Sr_{0.15})_{1-y}CuO_z\text{"} = y\,Na_2O + y\,CuO$$
$$+ (1 - y)\,Ca_{0.85}Sr_{0.15}CuO_2.$$
$$[A]$$
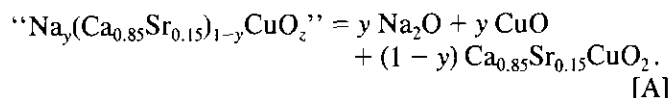
Note that the substitution of calcium by sodium is by no means excluded in oxide crystal chemistry. The ionic radius difference with calcium is 5%. In Aurivillius phases, for instance, $Bi_2NaNb_2O_{8.5}$, the sodium analogue of the classical compound $Bi_2CaNb_2O_9$, was recently reported (17). In addition, substitution of sodium for lanthanum, with a larger ionic radius difference, is known to occur in La_2CuO_4 (18).

But two facts must be borne in mind to understand the lack of sodium reaction with $Ca_{0.85}Sr_{0.15}CuO_2$ at ambient pressure. First, the $Ca_{0.85}Sr_{0.15}CuO_2$ structure has a very small and symmetrical unit cell and contains only rather light ions, with $3d$ ($4p$ for Sr^{2+}) as the outermost occupied electron level. It is therefore not as prone to deformations to accommodate size mismatches as structures containing larger, more polarizable cations such as La^{3+} or Bi^{3+}. This lack of flexibility is reflected in the very limited range of alkaline-earth solid solution in $Ca_{1-x}Sr_xCuO_2$ at ambient pressure ($\Delta x \leq 0.05$ (2, 19)). In addition, the composition $x = 0.15$ used here, which corresponds to that reported in earlier works (1, 14), appears to lie at the upper limit of the solid solution range. The incorporation in the lattice
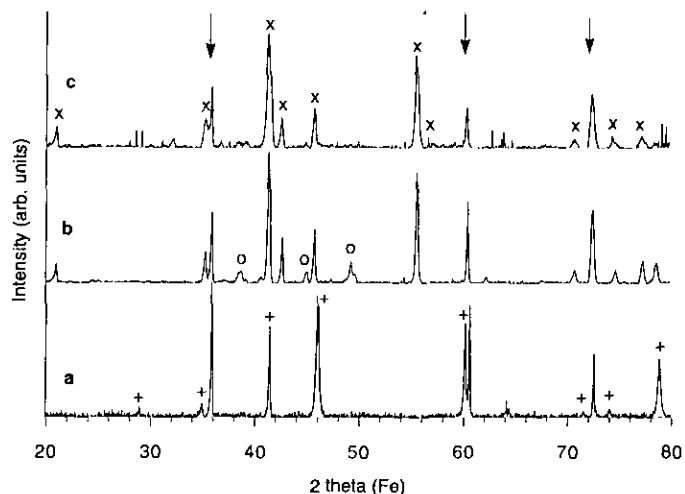

FIG. 2. Evolution of the X-ray powder pattern of $Ca_{0.85}Sr_{0.15}CuO_2$ on annealing under oxygen pressure. (a) Starting sample; (b) after treatment at 925°C, 150 atm O_2; (c) after further treatment at 700°C, 180 atm O_2. +, $Cu\infty$ phase; O, CuO; ×, orthorhombic phase; vertical arrows, Si standard lines.

of sodium, which is larger than the host site (see Table 1), is therefore not favored.

Second, $Ca_{0.85}Sr_{0.15}CuO_2$ has very slow kinetics of formation at ambient pressure. This barrier cannot be overcome by increasing the reaction temperature, due to the volatility of sodium oxide and its reactivity toward the crucible above ca. 900°C.

Oxygen Pressure Annealing

Alkali-metal substitution induces an increase in copper valence only if it is not compensated for by the introduction of oxygen vacancies in the structure. In $La_{2-x}Na_x CuO_{4-\delta}$, for instance, Shibata et al. (18) noted that an increase in x is accompanied by a simultaneous increase in δ; i.e., the effect of doping by an monovalent cation is partially canceled by the adjustment of oxygen vacancy concentration. This effect is not expected in the $Cu\infty$ structure, since all anionic sites in the alkaline-earth layers are already vacant. However, we investigated the behavior of doped and undoped $Ca_{0.85}Sr_{0.15}CuO_2$ under oxygen pressure.

Samples of $A_y(Ca_{0.85}Sr_{0.15})_{1-y}CuO_z$ ($A = $ Li, Na; $y = 0$ or 0.1) were annealed under 15–18 MPa oxygen pressure for 12 hr, initially at a temperature of $950 \pm 25°C$. The resulting X-ray diffraction pattern (Fig. 2) shows a partial decomposition of the $Cu\infty$ phase into CaO and $Ca_6Cu_7O_{14}$ (also known as $Ca_{0.85}CuO_2$), a compound with an orthorhombic structure related to that of $NaCuO_2$ (20, 21).

This reaction was studied in more detail. The transformation into $Ca_6Cu_7O_{14}$ occurs at all temperatures between 650 and 975°C, and is complete at 650–700°C. The reaction
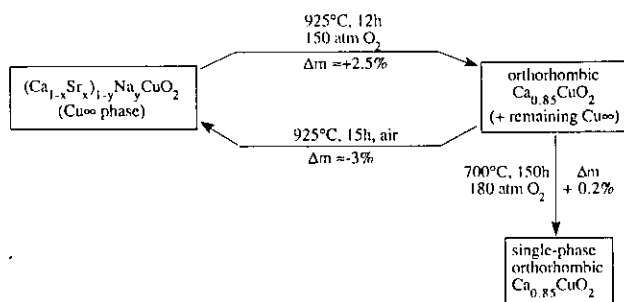
FIG. 3. Observed reaction paths on oxygen annealing.

mechanisms are summarized in Fig. 3. Several points deserve further attention:

1. The high-pressure reaction is always accompanied by a mass increase (Fig. 3). This result is in agreement with the oxygen uptake required to yield the stoichiometry $Ca_6Cu_7O_{14}$, corresponding to an average copper valence equal to 2.29. The theoretical mass change for the reaction

$$7\,Ca_{0.85}Sr_{0.15}CuO_2 + 0.525\,O_2 = (Ca, Sr)_6Cu_7O_{14} + 1.05\,CaO \quad [B]$$
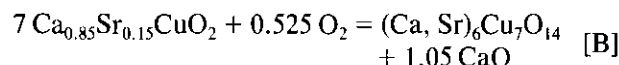
is 1.8%, compared to experimental values in the range 2–3%.

2. Reaction B is fully reversible, as shown in Fig. 3.

3. $Ca_{0.85}Sr_{0.15}CuO_2$ decomposes under oxygen pressure in spite of the fact that its density (4.95 g/ml) is larger than that of its high-pressure product $Ca_{0.85}CuO_2$ (4.51 g/ml). This shows that the driving force in this reversible transformation is the oxygen potential, not the total pressure. High oxygen pressures favor the orthorhombic, cation-deficient $NaCuO_2$-type phase because it requires a higher copper valence. In $Ca_6Cu_7O_{14}$, calcium deficiencies are an essential part of the structure and allow a relaxation of the cation sites, resulting in incommensurate superstructure (21).

CONCLUSION

This study has shown that hole doping in $Ca_{0.85}Sr_{0.15}$ CuO_2, either by tentative doping with alkali metals or by annealing in oxygen pressures up to 200 atm, is ineffective. Lithium probably enters the structure at the alkaline-earth site, as shown by the variation in X-ray reflection intensities as a function of nominal Li content. But this is not sufficient to induce superconductivity in this material, in spite of significant conductivity increases already observed on thin films.

The most interesting result observed in this work is the reversible transformation between the layered $Cu\infty$ structure and the chain-containing, $NaCuO_2$-type struc-

ture of $Ca_6Cu_7O_{14}$. The $Cu\infty$ phase has structural features in common with the superconducting series $A_2(Sr,Ba)_2$ $Ca_{n-1}Cu_nO_{4+2n+\delta}$, known to be p-type superconductors (A = Bi, Tl). But it lies on the "wrong" side of the transition line with $Ca_6Cu_7O_{14}$, i.e., on the high-temperature, low-oxygen-pressure side of the phase transition. Therefore no hole doping can be achieved in it.

In fact, it seems that holes can be forced into the $Cu\infty$ structure containing only the elements Ca, Sr, Cu, and O. Unlike the techniques used in the present study, this requires an elaborate combination of annealings under both mechanical pressure in excess of 5 GPa and an oxidizing atmosphere (6–9, 22). This route has not permitted the achievement of single-phase samples, and work is still under way to clearly identify the stoichiometry and structure of the superconducting component in the resulting mixtures, which contain compounds with various $Cu\infty$-related microstructures related to $Cu\infty$, not observed at low pressures (6, 7, 22).

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