

Stabilization of the Mixed Valence Cu(III)/Cu(IV) in the Perovskite Lattice of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ under High Oxygen Pressure

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A new mixed valence Cu(III)/Cu(IV) has been stabilized in the three-dimensional lattice of the perovskite-type oxide $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ ($0 \leq x \leq 0.25$). Chemical analysis and XPS studies confirm the mixed valence. This compound shows metallic properties with a broadening of the conduction band compared to that of LaCuO_3 . Such behavior can be explained either by the increase of the covalence of the average Cu-O bond or by the decrease of the structural distortion induced by the substitution of Sr(II) for La(III). No superconducting property has been detected in the material to temperatures as low as 4 K. © 1995 Academic Press, Inc.

Twenty years ago, Demazeau *et al.* stabilized for the first time six-coordinated Cu(III) in oxygen lattices derived from the perovskite structure, LaCuO_3 (1), $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ (1), and SrLaCuO_4 (2). The main objective of this research, devoted to the stabilization of the highest oxidation states of transition elements (3), was to correlate the modification of the physical properties of such oxides with the strong covalence of the Cu(III) oxygen bond.

In 1986, Müller and Bednorz observed superconducting behavior at a critical temperature (T_c) higher than that of conventional alloys (4) in a copper oxide with the K_2NiF_4 structure, $\text{Ba}_x\text{La}_{2-x}\text{CuO}_4$ with a mixed valence Cu(II)/Cu(III) (5). This discovery led to much research on copper oxides. The lattices which lead to the highest T_c were characterized by a strong bidimensionality (6) and a mixed valence for copper: Cu(III)/Cu(II) for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (7), $\text{La}_3\text{CuO}_{4+\delta}$ (8) ... or Cu(II)/Cu(I) in the case of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (9).

As yet, superconductivity has never been found in a copper oxide having a tridimensional lattice, either in those containing only Cu(III) (1, 2, 10, 11) or in those with a mixed valence Cu(III)/Cu(II) in the phase with the general formula $\text{LaCuO}_{3-\delta}$ (12) or $\text{La}_{1-x}\text{A}_x\text{CuO}_{3-\delta}$ (with $A = \text{Sr}$, $0.16 \leq x \leq 0.25$, and $\delta \approx 0.50$ (13-17), or $A = \text{Ba}$,

$x = 0.20$ and 0.50 , $\delta = 0.32$ and 0.67 (18-19)). Nevertheless, Khan (13) has claimed superconducting properties for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_{3-\delta}$ at $T < 50$ K. Unfortunately, this phenomenon was not reproducible; several studies on the same material have shown it has a metallic behavior (15, 17). The presence of an impurity with the global composition $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, quoted by Tokura *et al.* (17), could explain Khan's observations.

The strength of the Cu-O chemical bond plays an important role on the observed physical properties of oxides (3) and the objective of this research was to study the physicochemical behavior of a copper oxide with the perovskite-type structure and containing the mixed valence Cu(IV)/Cu(III); $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$. Oxygen pressure was an important tool to determine the oxygen stoichiometry of such an oxide (20).

Recently, a mixed valence has been stabilized in $\text{Sr}_2\text{CuO}_{4-\delta}$, resulting from an oxygen pressure treatment of Sr_2CuO_3 (21, 22).

I. PREPARATION OF OXIDES WITH THE GENERAL FORMULA $\text{Sr}_x\text{La}_{1-x}\text{CuO}_{3-\delta}$

Stabilization of the highest oxidation state of transition elements requires:

- (i) a relatively low reaction temperature and consequently very reactive initial compounds; and
- (ii) high oxygen pressures (3).

In order to prepare $\text{Sr}_x\text{La}_{1-x}\text{CuO}_3$ oxides, an amorphous starting product was used. Such material is obtained from the thermal decomposition of the corresponding solution of citrates in stoichiometric proportions as described by Chu *et al.* (23). As soon as the temperature reaches 800°C for $0.20 \leq x \leq 0.25$, the formation of a single phase (previously mentioned by Murayama *et al.* (14, 15) and Er-Rakho *et al.* (16)) is observed. The XRD patterns of these oxides can be indexed with a tetragonal cell (for example, for $x = 0.25$ the deviation from oxygen stoichiometry obtained from re-

dox back titration is $\delta = 0.47 \pm 0.02$ for $\text{Sr}_x\text{La}_{1-x}\text{CuO}_{3-\delta}$ and the cell parameters are $a = 10.81 \pm 0.01 \text{ \AA}$, $c = 3.849 \pm 0.005 \text{ \AA}$.

The objective of such a work being to get stoichiometric oxides, the last step of this synthesis was treatment under oxygen pressures. Two routes were possible:

(i) a two-step treatment under oxygen pressure, of the precursor obtained after calcination of 650°C . The first treatment is made in a reaction vessel connected to a compressed-gas apparatus in which the final pressure is limited to 500 bar because of the high temperature required for the synthesis, 900°C (20). Under such experimental conditions, only nonstoichiometric phases $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{3-\delta}$ are obtained. The structure is monoclinic for $0 < x \leq 0.15$ and always tetragonal for $0.20 \leq x \leq 0.25$ (14, 15). These phases can be, in a second step, treated under very high oxygen pressure ($P \approx 70 \text{ kbar}$) and at high temperature ($T \approx 900^\circ\text{C}$), using the thermal decomposition of KClO_3 in a belt-type apparatus (20).

(ii) The route developed for preparing stoichiometric oxides was an oxidizing treatment using high oxygen pressures in a belt-type apparatus ($P \approx 70 \text{ kbar}$, $T \approx 1000^\circ\text{C}$), after calcination of amorphous precursors following a method developed by Chu *et al.* (23) at 800°C . Due to the small domain of existence of the nonstoichiometric monoclinic and tetragonal phases, we have preferentially used this second route.

TABLE 1
Cell Parameters for $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$

x	$a_{\text{th}} (\text{\AA})$	$\alpha (^\circ)$	V/Z
0	5.431	60.85	57.72
0.05	5.428	60.84	57.61
0.10	5.427	60.83	57.57
0.15	5.425	60.77	57.43
0.20	5.432	60.65	57.50
0.25	5.456	60.09	57.53

II. CHEMICAL ANALYSIS AND X-RAY DIFFRACTION STUDY

The materials resulting from the second preparation route are, for $0 \leq x \leq 0.25$, isostructural with the rhombohedral form of LaCuO_3 (1, 24, 25). The cell parameters for several compositions in the interval $0 \leq x \leq 0.25$ are given in Table 1. Their variation versus x is schematized in Fig. 1. For $x = 0.25$, the α -angle is close to 60° ($\alpha \approx 60.09^\circ$), indicating a nearly cubic structure.

The Rietveld refinement of the XRD data does not allow a choice between the rhombohedral structure ($R_1 = 6.02$) and the cubic one ($R_1 = 6.68$) (R_1 is Bragg's reliability factor). Such a result is in agreement with a very small

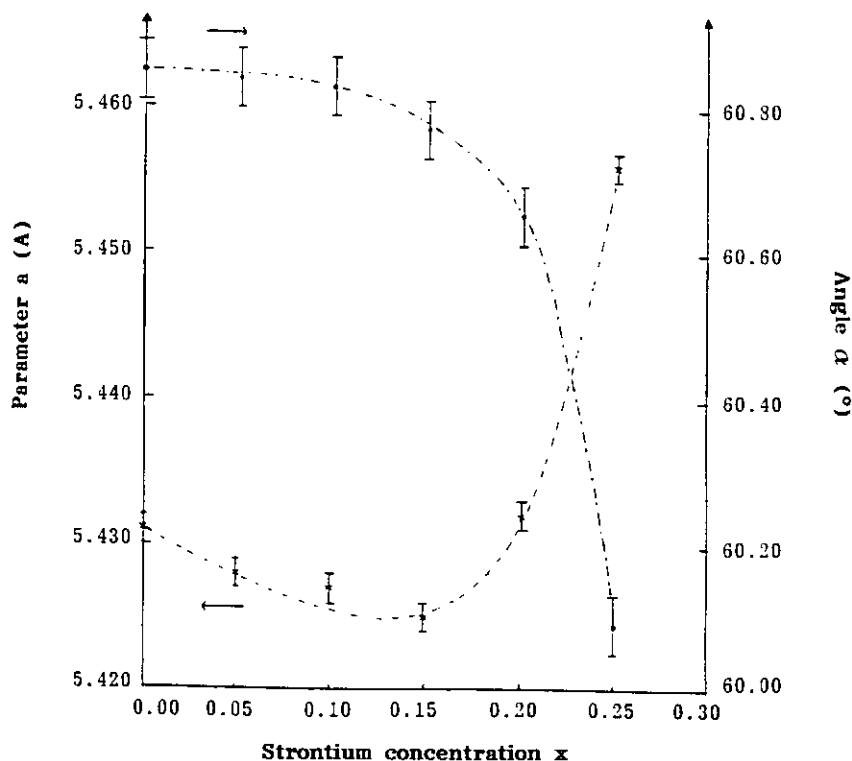


FIG. 1. Variation of the cell parameters versus the strontium rate x for the $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ system.

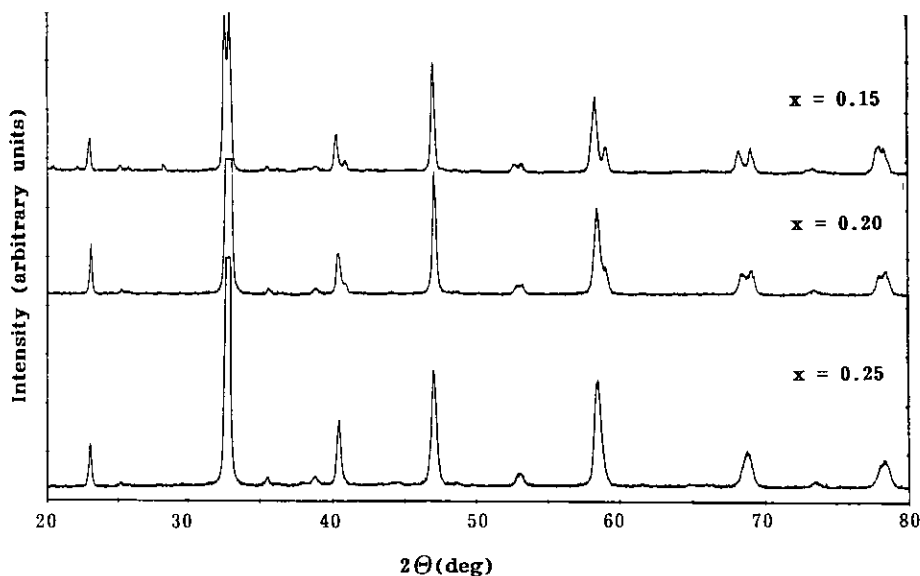


FIG. 2. Powder XRD spectra of the rhombohedral form of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ phase for $x = 0.15, 0.20,$ and 0.25 .

structural distortion difficult to resolve due to the domain of error for the calculated d spacings.

The decrease of the structural distortion can be explained both by the increase of the average ionic radius of the 12-coordinated cation induced by the substitution of Sr(II) ($r = 1.44 \text{ \AA}$) for La(III) ($r = 1.36 \text{ \AA}$) (26), and also by the corresponding enhancement of the average copper oxidation state, which decreases ionic radius.

For $x > 0.25$, two phases are observed in the X-ray diffractograms, one with the perovskite-type structure and the other one corresponding to CuO. Since the crystallographic parameters (a, α) of the perovskite phase are constant, $x = 0.25$ seems to be the upper limit for the substitution of strontium for lanthanum in the LaCuO_3 lattice. Figure 2 gives the XRD patterns of the rhombohedral form for $x = 0.15, 0.20,$ and 0.25 .

A thermogravimetry analysis has been carried out for two compositions $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ with $x = 0.10$ and 0.25 , the former in air or under argon atmosphere, the latter only in air (Fig. 3a).

For $x = 0.10$, with rising temperature, different structures isostructural with those described for the $\text{LaCuO}_{3-\delta}$ compounds are observed, as pointed out by Bringley *et al.* (12). The final plateau corresponds to a mixture of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and CuO (or Cu_2O at higher temperatures under argon atmosphere). An X-ray diffraction study versus temperature for the same composition ($\text{La}_{0.9}\text{Sr}_{0.10}\text{CuO}_3$) has led to the structural identification of the phase corresponding to each plateau (Fig. 4a). Close to 200°C , a tetragonal phase is detected with a small domain of stability. Near 300°C the monoclinic structure takes place. Such a structure is stable up to 780°C . At higher temperatures, the orthorhombic structure is then stabilized. This thermal structural evolution observed for

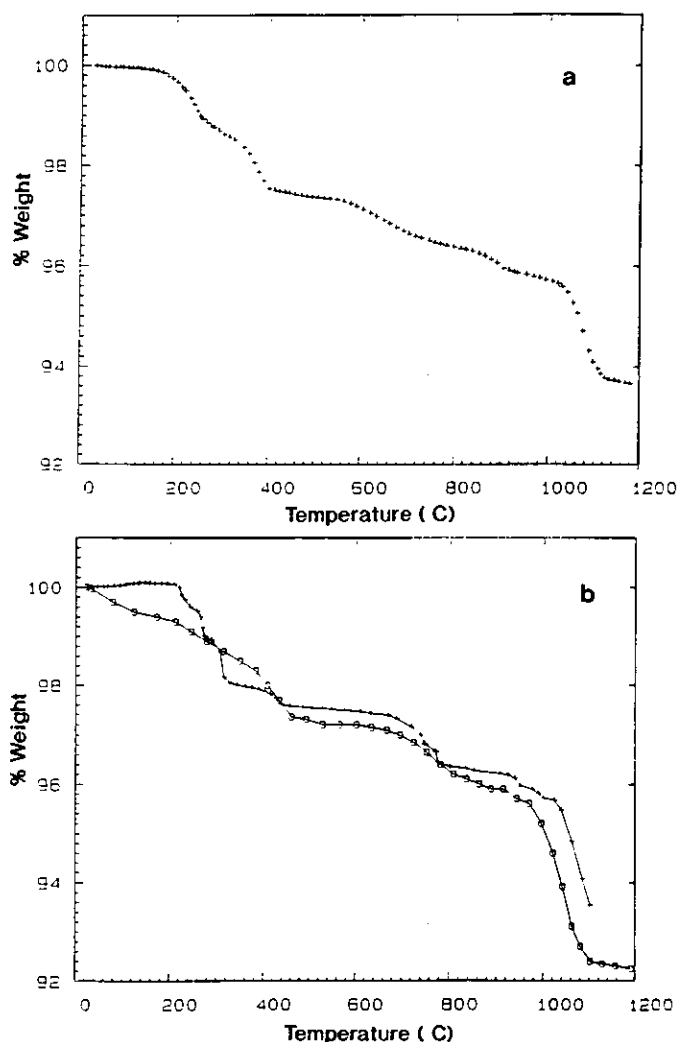


FIG. 3. TGA curves for two samples: $\text{La}_{0.90}\text{Sr}_{0.10}\text{CuO}_3$ under argon atmosphere (a); $\text{La}_{0.90}\text{Sr}_{0.10}\text{CuO}_3$ (+) and $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_3$ (o) in air (b).

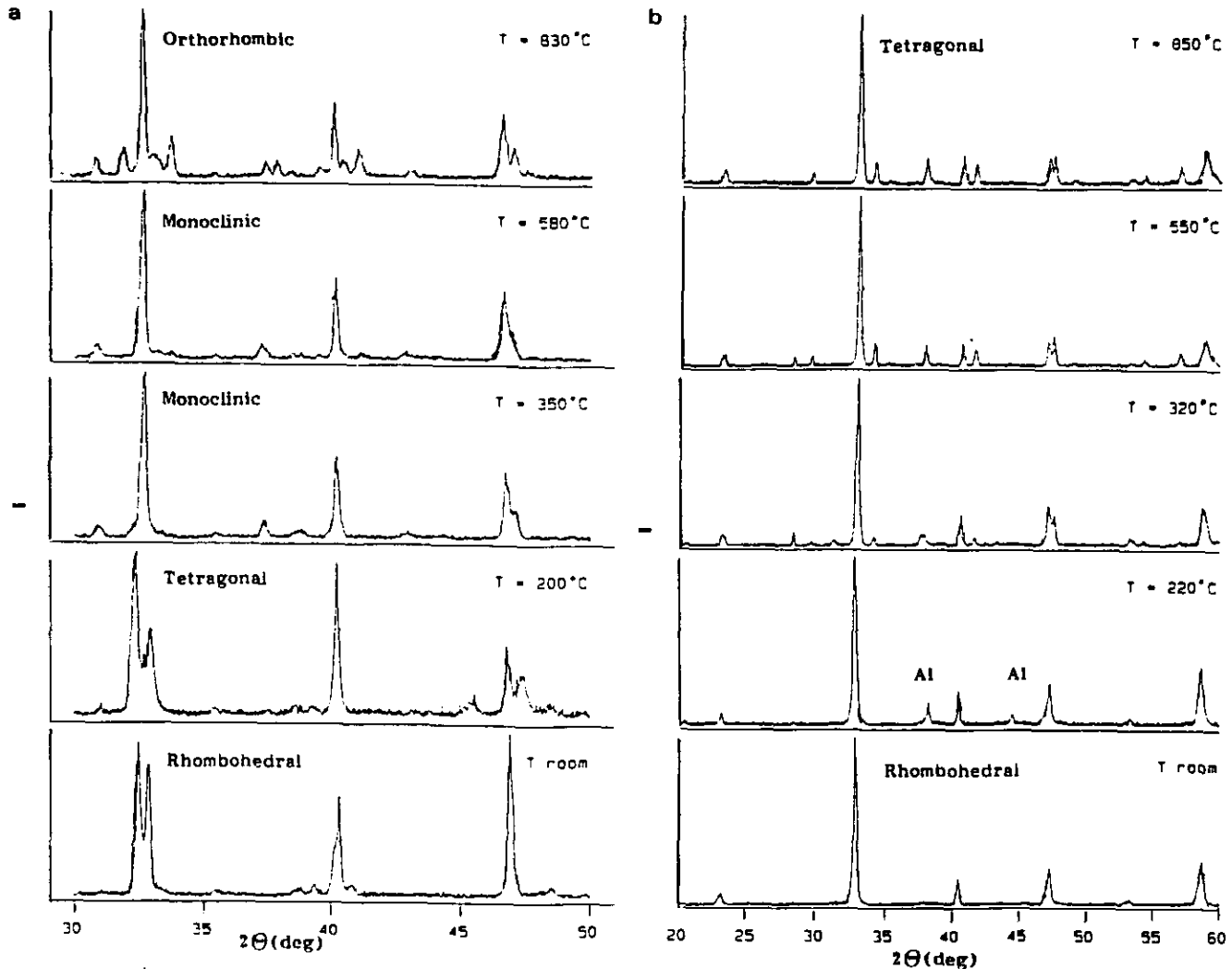


FIG. 4. Powder XRD spectra versus temperature of $\text{La}_{0.90}\text{Sr}_{0.10}\text{CuO}_3$ (a) and $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_3$ (b) phases.

$\text{La}_{0.9}\text{Sr}_{0.10}\text{CuO}_3$ is in agreement with that described by Bringley *et al.* (27) for tetragonal LaCuO_3 .

For $x = 0.25$, with rising temperature, only one phase is observed. Its structure corresponds to the tetragonal one described by Murayama *et al.* and Er-Rakho *et al.* (See Ref. 14, 15, 16 and Fig. 4b). This result is surprising if we compare the TGA graphs between both phases $x = 0.10$ and 0.25 , which show almost the same plateaus. The more gradual oxygen loss observed in the TGA curve for the tetragonal phase $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{3-\delta}$, as well as the higher strontium content, probably explain the high-temperature XRD diagrams. A high strontium concentration does not favor the stabilization of Bringley's phases.

The total loss of oxygen has led to the evaluation of the oxygen composition: $\text{La}_{0.90}\text{Sr}_{0.10}\text{CuO}_{3.01 \pm 0.02}$. This result has been confirmed by TGA under an Ar-H_2 atmosphere: $\text{La}_{0.90}\text{Sr}_{0.10}\text{CuO}_{3.00 \pm 0.03}$.

III. MAGNETIC AND ELECTRIC STUDIES

Figure 5 depicts the thermal evolution of the reciprocal molar magnetic susceptibility [$\chi_M^{-1} = f(T)$] for different compositions of the $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ phase, after correction for the diamagnetic contribution of each atom. The very small variation of the χ_M' value in the investigated domain of temperature ($5 \leq T \leq 290$ K) suggests a Pauli paramagnetic behavior. In addition, for the same temperature, the change of χ_M' versus the chemical composition x is small. Nevertheless, a small increase can be detected.

The electrical properties versus temperature have been measured with the four-point technique on pellets compressed at $P \approx 1400$ bar and at room temperature in order to avoid the formation of oxygen vacancies at high temperature.

The resulting measurements (Fig. 6) reveal a slight de-

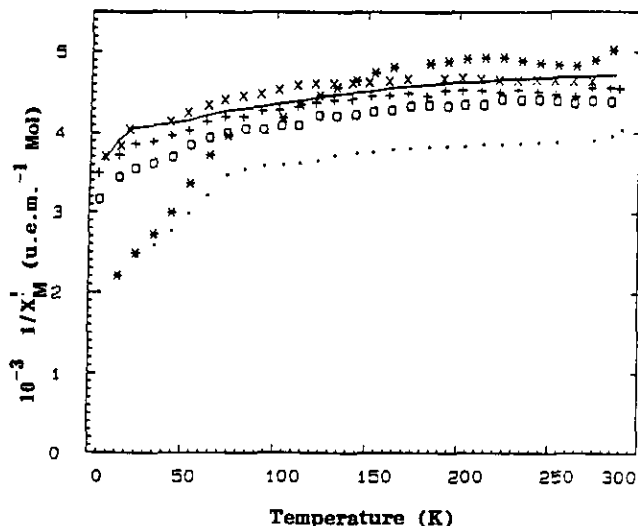


FIG. 5. Thermal variation of the reciprocal molar magnetic susceptibility of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ rhombohedral phase with $x = 0$ (—); 0.05 (×); 0.10 (+); 0.15 (○); 0.20 (*), and 0.25 (●).

crease of the conductivity as a function of temperature for a specific composition x . Furthermore, at constant temperature, a small decrease of σ versus x can be observed.

IV. XPS STUDY

The substitution of Sr(II) for La(III) induces the formal stabilization of copper (IV), and so two types of Cu–O bonds could exist in the $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ lattice. XPS measurements have been performed on two samples; one

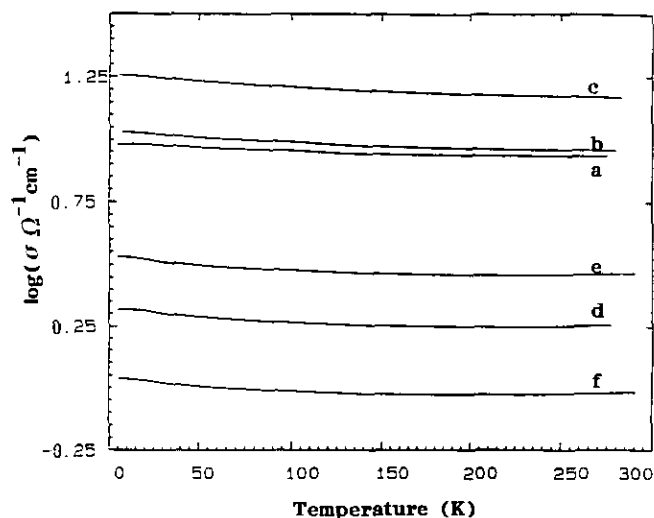


FIG. 6. Thermal variation of the conductivity of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$ rhombohedral phase (a) $x = 0$; (b) $x = 0.05$; (c) $x = 0.10$; (d) $x = 0.15$; (e) $x = 0.20$; and (f) $x = 0.25$.

with the composition $\text{La}_{0.80}\text{Sr}_{0.20}\text{CuO}_3$ and the other LaCuO_3 (as reference), with a Perkin–Elmer PH1-5100 spectrometer (resolution 0.2 eV). A monochromatic radiation MgK_α (1253.6 eV) has been used. The pressure inside the experimental chamber was close to 2×10^{-10} Torr. The etching was carried out with Ar ions under the following conditions: 1 KeV, 25 mA, and 2×10^{-10} Torr. The observed binding energies (BE) were corrected from the known reference (BE of C 1s: 284.6 eV).

For LaCuO_3 , where the oxidation state of copper determined from chemical titration is 3.00 ± 0.02 , the BE corresponding to Cu $2p_{3/2}$ is found to be ≈ 933.5 eV (Fig. 7) without any modifications before and after the Ar ion bombardment, indicating that the Cu(III) only is stabilized in the LaCuO_3 lattice. Previously an XPS study on LaCuO_3 (31) led to a highest value (936.7 eV). Such a difference could be due to the calibration. In our case the observed BE is approximately 1 eV lower than the values reported in literature: 934.7 eV for Cu(III) $2p_{3/2}$, 934.2 and 934.9 eV for $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ (28–30); 934.6 eV for NaCuO_2 (31), and 934.7 eV for $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$ (32).

These values can be discussed as a function of the local symmetry for Cu(III) and the electronic properties (electronic localization or delocalization) for the corresponding oxide. The value observed for LaCuO_3 [six-coordinated Cu(III)] seems lower than in NaCuO_2 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ [Cu(III) in square planar]. This fact can be explained by the higher covalence of the (Cu–O) bond in a square planar site. In the case of $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$, which structure is related to that of K_2NiF_4 , the electron localization and the symmetry of the copper site (nearly square planar, $c/a = 3.54$ due to the low-spin d^8 configuration) lead to a high BE value (934.7 eV).

The XPS spectra obtained for $\text{La}_{0.80}\text{Sr}_{0.20}\text{CuO}_3$ are given in Figs. 8a and 8b, before and after Ar ion bombard-

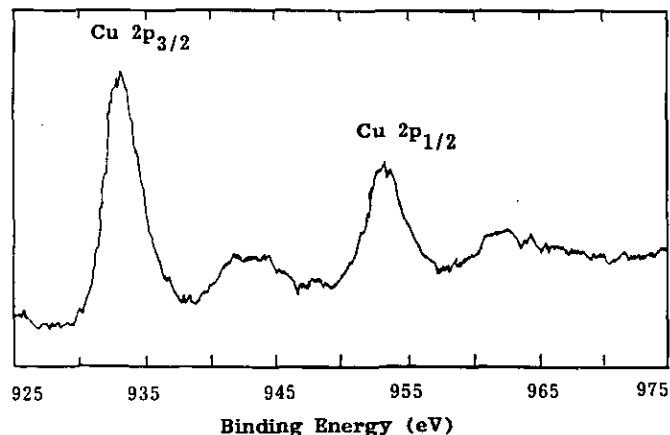


FIG. 7. X-ray photoelectron spectrum of the Cu $2p_{3/2}$ peak for LaCuO_3 .

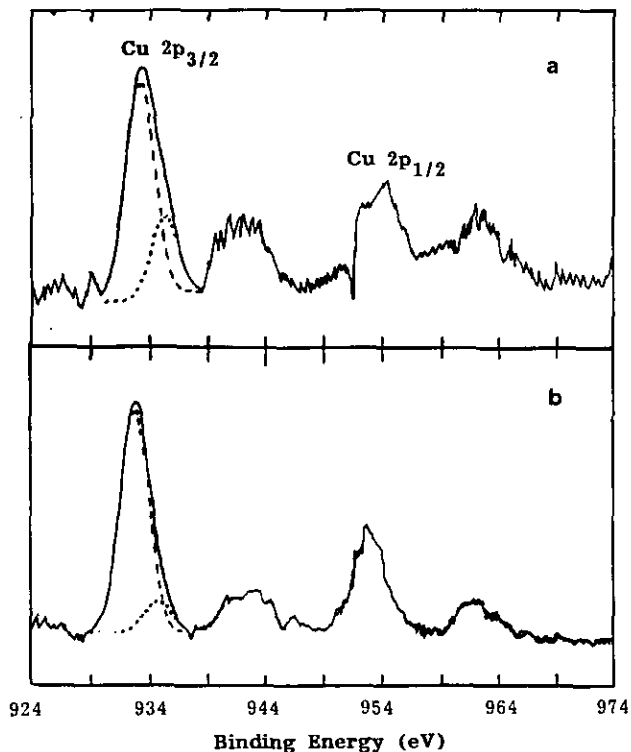


FIG. 8. X-ray photoelectron spectra of the $\text{Cu } 2p_{3/2}$ peak. Deconvolution of the peak for $\text{La}_{0.80}\text{Sr}_{0.20}\text{CuO}_3$ before (a) and after the argon ion etching (b).

ment. Due to the significant change in full width at half maximum ($\Delta E \approx 3.64$ eV) in both cases, the corresponding $\text{Cu } 2p_{3/2}$ peak has been analyzed in two parts. Before etching, the corresponding values are respectively close to 933.1 and 935.3 eV. The BE value close to 933.1 eV can be attributed to Cu(III) in an octahedral site of the lattice characterized by a strong electronic delocalization, if we compare with LaCuO_3 (BE = 933.5 eV). The highest BE value (935.3 eV) can involve a higher copper oxidation state, as six-coordinated Cu(IV). After etching, the observed BE values are respectively 933.3 and 935.6 eV. After deconvolution, the resulting peaks can give an evaluation of the different copper species close to the surface (i) before etching 75% (BE \approx 933.1 eV) and 25% (BE \approx 935.3 eV); (ii) after etching: 88% (BE \approx 933.3 eV) and 12% (BE \approx 935.6 eV). The experimental value before etching is close to the starting stoichiometry ($\text{La}_{0.80}\text{Sr}_{0.20}\text{Cu(III)}_{0.80}\text{Cu(IV)}_{0.20}\text{O}_3$). The decrease of Cu(IV) content after etching could be attributed to (i) an instability of such formal oxidation state or (ii) a nonhomogeneity of Cu(IV) formation in the lattice. The stabilization of such a Cu(IV) oxidation state resulting from oxygen diffusion under pressure conditions, its stabilization would be favored near the surface of the grains.

The analysis of these experimental results suggests the

presence of two different copper oxidation states ($\Delta E \approx 2$ eV) in the $\text{La}_{0.80}\text{Sr}_{0.20}\text{CuO}_3$ lattice.

CONCLUSIONS

This study has underlined the possibility to stabilize a new mixed valence Cu(III)/Cu(IV) in the perovskite-type lattice of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_3$. TGA and XPS studies have confirmed (i) an average oxidation state higher than (III) and (ii) the existence of two different Cu–O bonds through the observation of two $\text{Cu } 2p_{3/2}$ BE values. One corresponds to Cu(III) in a metallic lattice (933.3 ± 0.20 eV), and the other, characterized by a higher BE value (935.5 ± 0.20 eV), is attributed to another valence state higher than III+: Cu(IV).

The observed physical properties are consistent with the competition between two factors:

(i) a broadening of the conduction band induced by either the increase of the covalence of the average Cu–O bond or the decrease of the structural distortion of the perovskite lattice;

(ii) a local ferromagnetic-type interaction between Cu(III) and Cu(IV) due to the presence of holes in the conduction band resulting from the Cu(IV) stabilization.

These factors are in favor of a metallic conductivity, but no superconducting behavior has been observed.

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