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The Great Flexibility of the Rock Salt Layers in the Lead-Based 1212 High-Tc Superconductive Cuprates: The Oxides (Pb, A)Sr_2(Ca, Ln)$Cu_2O_{7-\delta}$

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A systematic investigation of superconductivity based on 1212-type cuprates with nominal compositions $(Pb_{0.5}A_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ with A = Cu, Zn, Ni, Mg, Cd, Ca, Sr and $(Pb_{0.7}A_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ with A = Sc, Fe has been carried out. It has been demonstrated that the different A cations enter into the structure, mainly in the rock salt type slabs, forming $[(Pb_{1-x}A_x)O]_\infty$ layers with an A content smaller than the nominal one. The study of the superconducting properties of these phases, and especially of their annealing properties at low temperature, shows that the critical temperatures of these phases, ranging from 30 to 90 K, are closely related to the nature of the A cations. The replacement of Y by Yb is also investigated. These results are discussed in terms of the size of the A cations, the oxygen nonstoichiometry, and the possible coexistence of the couples Pb(II)/Pb(IV) and Cu(II)/Cu(III).

Introduction

The discovery of superconductivity in the lead-based 1212 cuprate, $Pb_{0.5}Sr_{2.5}(Ca_{1-x}Y_x)Cu_2O_{7-\delta}$ (*1*, *2*), has opened the route to investigations, since a Tc (onset) of 90 K could be reached. However, up to now, several issues remained unanswered. The first one deals with the very broad character of the transition, which can be interpreted as an inhomogeneous distribution of oxygen and vacancies, but so far has not been optimized. The second issue concerns the localization of strontium and knowledge of the oxygen content. Several attempts to solve this structure by X-ray diffraction and neutron diffraction were made; they suggested that excess strontium was localized in the rock salt layers. Nevertheless, the rather high values of the R factor and the abnormally short Sr–O distances make these preliminary results not completely convincing. The third point focused on is the possible introduction of various cations in the rock salt layers at the same sites as lead, i.e., instead of strontium. Indeed, strontium could be replaced by calcium (3), leading to a Tc (offset) of 60 K, whereas the copper oxide (Pb, Cu)Sr_2(Ca, Y)$Cu_2O_{7\pm\delta}$, first synthesized by Subramanian *et al.* (4), could be made superconducting with a Tc of 40–60 K by annealing under oxygen pressures ranging from 5 to 150 bar (*5*, *6*) or by high temper-

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ature quenching (*7–10*), or by optimization of the Ca : Y ratio (*11*). After these first results several other substitutions by indium (*12*) and cadmium (*13*) also showed a possibility of obtaining a Tc ranging from 45 to 70 K. In order to understand these different points, we have performed a systematic study of the introduction of various metallic elements besides lead into the rock salt layers. We present here the results obtained for the series of cuprates (Pb, A)Sr_2(Ca, Y) $Cu_2O_{7\pm\delta}$ with A = Cu, Mg, Zn, Ni, Fe, Sc, Cd, Ca, Sr, and for some of them we discuss the possible influence of the replacement of Y by Yb on superconductivity.

Experimental

Sample Preparation and Characterization

Samples with the nominal compositions of $(Pb_{0.5}A_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ (A = Cu, Mg, Zn, Ni, Cd) and $(Pb_{0.7}A_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ (A = Sc, Fe, Cu) were prepared by mixing the oxides PbO_2/AO (A = Cu, Mg, Zn, Ni, Cd) or PbO_2/A_2O_3 (A = Sc, Fe), SrO_2, Sr_2CuO_3, CaO, and Y_2O_3 in the appropriate molar ratios in order to maintain the oxygen content equal to 7. For A = Ca, Sr the synthesis conditions have been previously described (*1, 3*) and may involve oxygen amounts varying between 6.75 and 7.50.

In all cases, the mixtures were finely ground in an agate mortar and compressed under a pressure of 1 ton/cm^2 by bars of dimensions 12 × 2 × 2 mm^3. The bars were placed in alumina crucibles and heated in evacuated quartz ampoules at 880°C for 12 hr. The samples were then quenched to RT and characterized by X-ray diffraction analysis using Cu $K\alpha$ radiation.

The chemical compositions of the individual microcrystallites of the as-synthesized specimens were examined by energy-dispersive X-ray spectrometry (EDS) by means of a TOPCON2B electron microscope operating at 200 kV.

Some of the bars were annealed at temperatures ranging between 400 and 900°C for times varying from 10 to 60 hr. Firings were carried out at oxygen pressures of 5, 10, 20, 30, 40, 50, 70, and 100 bar in a commercial high-pressure furnace to make the samples superconducting by adjustment of oxygen. In the case of cadmium-based 1212 compounds superconductivity was more particularly enhanced after subsequent annealings at 970°C in gold foil for 3 hr in oxygen as described elsewhere (*13*).

Magnetic and Electrical Properties

The magnetic properties of the samples were measured with an ac susceptometer (Lake Shore) using an ac excitation field of 0.5 mT at 80 Hz without a dc component. The $\chi'(T)$ curves allowed us to study the variations of T_c and of the superconducting volume with the annealing temperature, the annealing time, and the oxygen pressure.

Electrical resistivity measurements were made with a standard four-probe technique with measuring currents of 0.01–1 mA.

Results and Discussion

The synthesis of absolutely pure phases has not been possible whatever the nominal composition and the thermal treatments. The powder X-ray patterns of most of the samples reveal, besides the 1212-type phase, crystallized impurities whose nature depends on the nominal composition and on the synthesis process and subsequent annealings ($SrCO_3$, $SrCuO_2$, Sr_2CuO_3, $Sr_{14-x}Ca_xCu_{24}O_{41}$, $Pb_3CuSr_5O_{12}$, etc. . .). The existence of such crystallized impurities is confirmed by a systematic electron diffraction exploration, and their amount can be estimated in the range from 5 to 10%. Moreover, the E.D. investigation shows that, even if the samples seems to be very pure from the XRD analysis, a substantial number of particles are amorphous or very poorly crystallized. These preliminary observations are of capital importance for interpretation of the superconducting properties of these materials.

The As-synthesized Samples (Pb, A) $Sr_2(Ca, Y)Cu_2O_{7-\delta}$

The oxides $(Pb_{0.50}A_{0.50})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ could be prepared with a majority in the 1212 phase (i.e., >90%) for A = Cu, Mg, Cd, Zn, Ni, and this was confirmed for A = Ca, Sr corresponding to the superconductors previously described (*1–3*). For A = Fe(III), Sc(III), the best results were obtained for the compositions $(Pb_{0.7}A_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$.

All these phases were indexed in a tetragonal cell with the parameters given in Table I. It can be seen that the latter do not vary dramatically with the nature of the A cation; the cell volume remains approximately constant. One observes, in particular, that the "$Pb_{0.5}Ca_{0.5}$" and "$Pb_{0.5}Sr_{0.5}$" compounds exhibit the smaller parameters despite the greater size of calcium and strontium with respect to other A cations. This might be due to a variation of the oxygen content δ from one oxide to the other. However, the existence of impurities, besides the 1212-phase and an amorphous phase, makes the introduction of the A cations in the structure questionable. In order to answer this question a systematic EDS analysis combined with electron diffraction was carried out on several samples.

Two compounds with nominal compositions, $(Pb_{0.7}Cu_{0.3})Sr_2(Y_{0.85}Ca_{0.15})Cu_2O_{7-\delta}$ and $(Pb_{0.5}Cd_{0.5})Sr_2YCu_2O_{7-\delta}$, were investigated as references. The first one was chosen because its structure has been studied previously from single crystals (*4, 14*), whereas the second is of interest because of a simpler formula which does not involve calcium. Besides these two compounds, five samples with the nominal composition $(Pb_{0.5}A_{0.5})Sr_2(Y_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$ were studied for A = Cd, Sr, Mg. The analytical results summarized in Table II allow the following comments to be made:

(i) Only one sample, $(Pb_{0.7}Cu_{0.3})Sr_2(Y_{0.85}Ca_{0.15})Cu_2O_{7-\delta}$, is characterized by a chemical composition close to the nominal composition. This result is in agreement with the single crystal study performed by Subramanian *et al.* (*4*).

(ii) In all the samples containing calcium, one always observes a calcium deficiency and excess yttrium with respect to the nominal composition.

(iii) In all the oxides containing cadmium one observes a cadmium deficiency with respect to the nominal composition.

TABLE I

LATTICE PARAMETERS AND TC'S OFFSET (R = 0) FOR THE Pb-BASED 1212 CUPRATES

Nominal composition 1212	a (Å)	c (Å)	V(Å^3)	Tc(R = 0) optimized (°K)	Ref.
$(Pb_{0.5}Cu_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.824(2)	11.880(2)	173.72	42–60	(*5*)–(*6*)
$(Pb_{0.5}Mg_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.8249(1)	11.9237(4)	174.44	40	This work
$(Pb_{0.5}Cd_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.8195(2)	11.9543(9)	174.39	60	This work
$(Pb_{0.5}Ca_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.8141(4)	11.916(3)	173.35	50–60	(*3*)
$(Pb_{0.5}Sr_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.8166(6)	11.907(4)	173.44	60–75	(*1, 2*)
$(Pb_{0.5}Tl_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.815(2)	11.996(2)	174.59	44	(*15, 16*)
$(Pb_{0.7}Sc_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.8265(2)	11.9303(7)	174.68	38	This work
$(Pb_{0.7}Fe_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.8308(7)	11.834(3)	173.59	nonsuperconducting	This work
$(Pb_{0.5}Ni_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7\pm\delta}$	3.8243(4)	11.925(2)	174.40	nonsuperconducting	This work

TABLE II

EDS ANALYSIS OF SOME 1212 CUPRATES (Pb, A)Sr_2(Ca, Y)$Cu_2O_{7-\delta}$

Nominal Compositions		Analytical results: Possible cationic distribution
$Pb_{0.7}Cu_{0.3}Sr_2(Y_{0.85}Ca_{0.15})Cu_2O_{7-\delta}$		$(Pb_{0.68}Cu_{0.30}Ca_{0.02})Sr_2(Y_{0.89}Ca_{0.11})Cu_2O_{7-\delta}$
$Pb_{0.5}Cd_{0.5}Sr_2YCu_2O_{7-\delta}$		$(Pb_{0.55}Cd_{0.22}Cu_{0.23})Sr_2(Y_{0.93}Cd_{0.07})Cu_2O_{7-\delta}$
$Pb_{0.5}Cd_{0.5}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{7-\delta}$		$(Pb_{0.59}Cd_{0.05}Sr_{0.13})Sr_2(Y_{0.65}Ca_{0.23}Cd_{0.12})Cu_2O_{7-\delta}$
$Pb_{0.5}Mg_{0.5}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{7-\delta}$	*A*	$(Pb_{0.61}Mg_{0.07}Cu_{0.28}Ca_{0.04})(Sr_{1.92}Ca_{0.08})(Y_{0.70}Ca_{0.30})Cu_2O_{7-\delta}$
	B	$(Pb_{0.60}Mg_{0.17}Cu_{0.21}Sr_{0.02})Sr_2(Y_{0.56}Ca_{0.44})Cu_2O_{7-\delta}$
$Pb_{0.5}Sr_{0.5}Sr_2Y_{0.5}Ca_{0.5}Cu_2O_{7-\delta}$	*A*	$(Pb_{0.66}Sr_{0.34})Sr_2(Y_{0.60}Ca_{0.21}Sr_{0.19})Cu_2O_{7-\delta}$
	B	$(Pb_{0.64}Sr_{0.16}Cu_{0.20})Sr_2(Y_{0.60}Ca_{0.32}Sr_{0.07})Cu_2O_{7-\delta}$

Note. A and *B* relate to two different preparations of the samples.

(iv) The A cation content is generally smaller than that of the nominal composition. Moreover, it depends on the thermal treatment. Nevertheless, the amount of the A cation introduced into the crystals is significant in all cases.

Investigation of the magnetic susceptibility of the as-synthesized phases shows that all the oxides "$Pb_{1-x}A_x$" characterized by small A cations, i.e., A = Cu, Mg, Zn, Sc, Fe, Ni, do not superconduct, whereas the oxides "$Pb_{0.5}A_{0.5}$" involving larger cations, i.e., A = Cd, Ca, Sr, exhibit superconductivity. In the three cases the transitions are very broad and the superconducting volume is weak, but nevertheless is characteristic of bulk superconductivity.

Effect of Oxygen Annealing

The previous studies of the oxides $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ and $(Pb_{0.5}Sr_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ (*5*, *2*) have shown that the superconducting properties of these two oxides can be dramatically improved by annealing under various oxygen pressures. We have also tried to optimize the superconducting properties of the oxides of nominal composition $(Pb_{0.5}A_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ with A = Mg, Zn, Cd, Ni and $(Pb_{0.7}A_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ with A = Sc, Fe synthesized above, by annealing at 400°C under different oxygen pressures.

No superconductivity could be induced in the Ni and Fe cuprates, whatever the oxygen pressure ranging from 10 to 100 bar, and the annealing temperature ranging from 400 to 900°C. Although negative, this result is important when one takes into consideration the fact that in all other phases superconductivity could be either induced or enhanced. This behavior can be explained by the ability of iron and nickel to take a pyramidal coordination so that these cations will sit not only in the Pb sites but will tend to substitute for copper in the CuO_5 pyramids (Fig. 1), killing superconductivity. Conse-

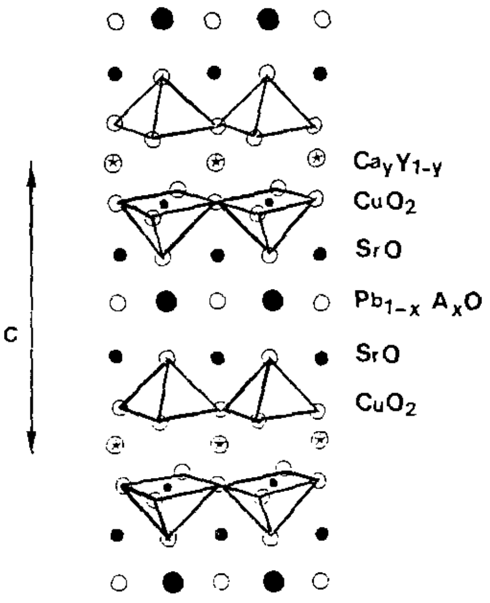

FIG. 1. Schematic drawing of the 1212-type layered structure projected along **b**.

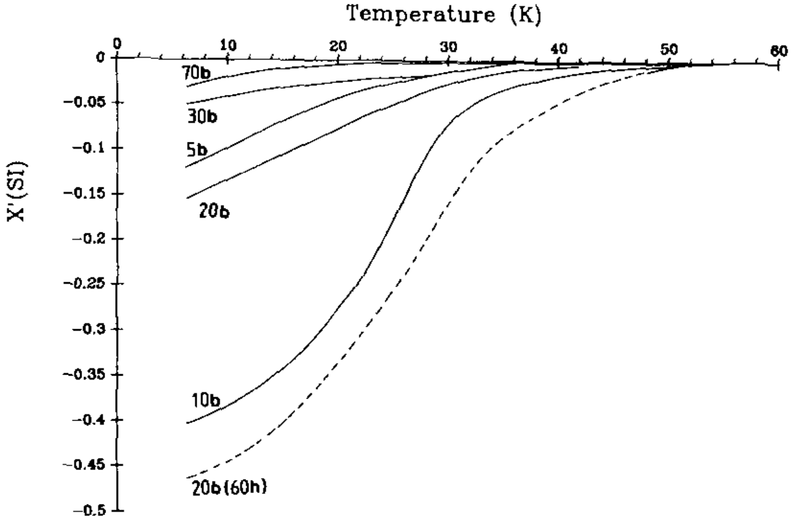

FIG. 2. AC susceptibility curves for samples of nominal composition $(Pb_{0.5}Mg_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ annealed at 400° C for 10 hr at oxygen pressures of 5, 10, 20, 30, and 70 bar. The lower curve (dotted line) corresponds to an annealing time of 60 hr at $pO_2 = 20$ bar.

quently, the cationic distribution in these phases should be intermediate between the limit formula:

$(Pb_{0.5}Ni_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ and
$(Pb_{0.5}Cu_{0.5})Sr_2(Ca_{0.5}Y_{0.5})(Cu_{1.5}Ni_{0.5})Cu_2O_{7-\delta}$,
$(Pb_{0.7}Fe_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ and
$(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})(Cu_{1.7}Fe_{0.3})O_{7-\delta}$.

The behavior of Mg, Zn, and Sc cuprates is similar to that $(Pb_{0.7}Cu_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_{7-\delta}$ (*5*). Superconductivity is induced in these compounds by annealing these phases under oxygen pressure. In the series, the transition is rather broad (Fig. 2–4). However, it is worth pointing out that the Zn

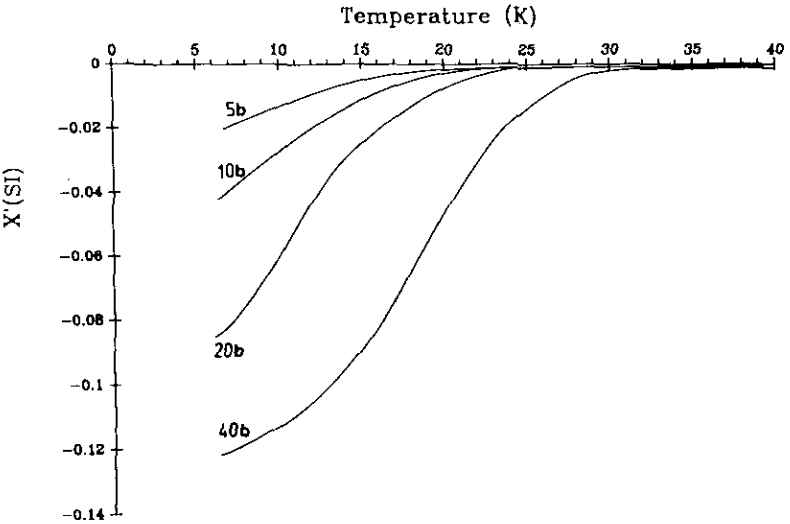

FIG. 3. AC susceptibility curves for samples of nominal composition $(Pb_{0.5}Zn_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ annealed at 400°C for 10 hr at oxygen pressures of 5, 10, 20, and 40 bar.

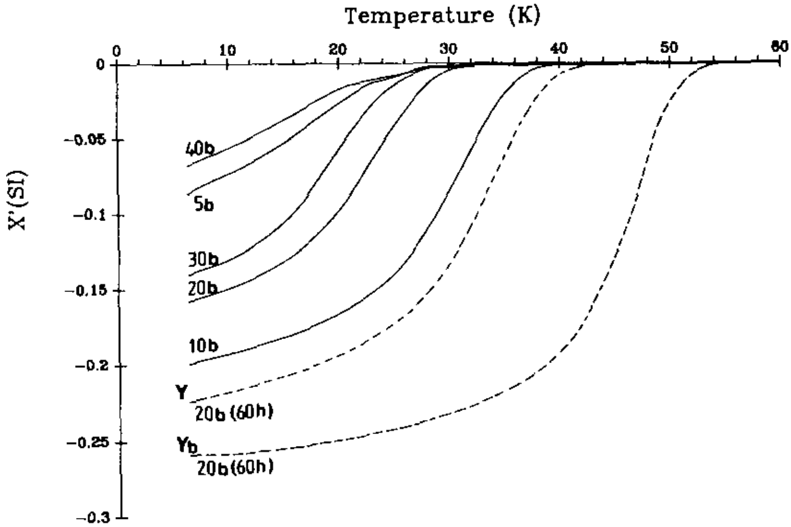

FIG. 4. AC susceptibility curves for samples of nominal composition $(Pb_{0.7}Sc_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ annealed at 400°C for 10 hr at oxygen pressures of 5, 10, 20, 30, and 40 bar. The lower curves correspond to samples of $(Pb_{0.7}Sc_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ (curve a) and $(Pb_{0.7}Sc_{0.3})Sr_2(Ca_{0.5}Yb_{0.5})Cu_2O_7$ (curve b) annealed at 400° C for 60 hr at pO_2 = 20 bar.

compound exhibits poor superconducting properties (Fig. 3) compared to Mg and Sc oxides (broad transition, low superconducting volume, and maximum Tc's of 30 K). The critical temperature of the Sc compound (40 K), (Fig. 4) is smaller than that of the Mg phase (50 K) (Fig. 2), but the transition is much narrower, especially for the sample annealed under 20 bar for 60 hr. The evolution of Tc's versus oxygen pressure for A = Mg, Sc (Fig. 5) shows that there exists an optimal oxygen pressure allowing the maximum value of Tc's to be reached. This result is in agreement with those previously observed for A = Sr and Ca (*1–3*).

The optimization of cadmium cuprates is very different. Annealings at 400°C, under different oxygen pressures, do not change the superconducting properties. On the other hand, annealings at 900°C under oxygen pressures $p_{O_2} \geq 50$ bar increase both the superconducting volume and the Tc's (Fig. 6). But the best results are obtained by wrapping the sample in gold foil and annealing it at 970°C in an oxygen flow (3 liters/hr); one obtains (Fig. 6) a Tc of 60 K and a full (140%) shielding signal at 5 K. The resistance measurements (Fig. 7) confirm that Tc increases

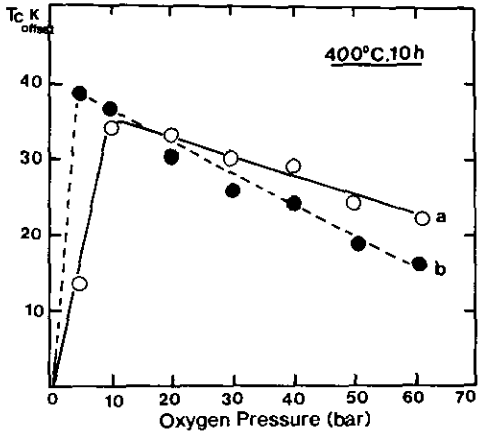

FIG. 5. Variation of Tc versus the oxygen pressure applied during the annealing of the 1212 phases $(Pb_{0.5}Mg_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ (curve a) and $(Pb_{0.7}Sc_{0.3})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ (curve b) at 400°C for 10 hr.

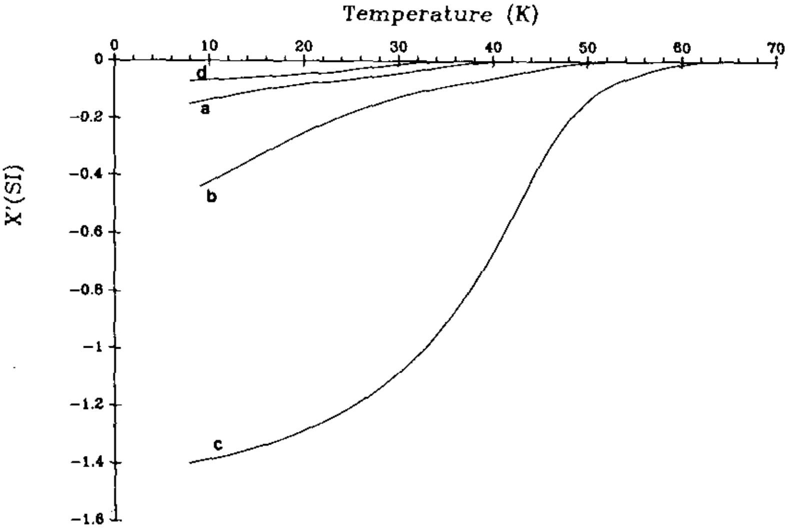

FIG. 6. AC susceptibility curves for samples of nominal composition $(Pb_{0.5}Cd_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ annealed (a) at 900° in air for 10 hr, (b) at 900° for 10 hr at pO_2 = 50 bar, and (c) at 970°C in gold foil for 3 hr in O_2 flow. Curve d corresponds to the as-synthesized samples in the evacuated quartz tube.

from 24 up to 60 K by annealing at 900–970°C; moreover, one observes that the conductivity of the normal state increases significantly from a semiconducting to a metallic state. This peculiar behavior of cadmium cuprates, which require higher annealing temperatures compared to the other 1212 cuprates, suggests that superconduc-

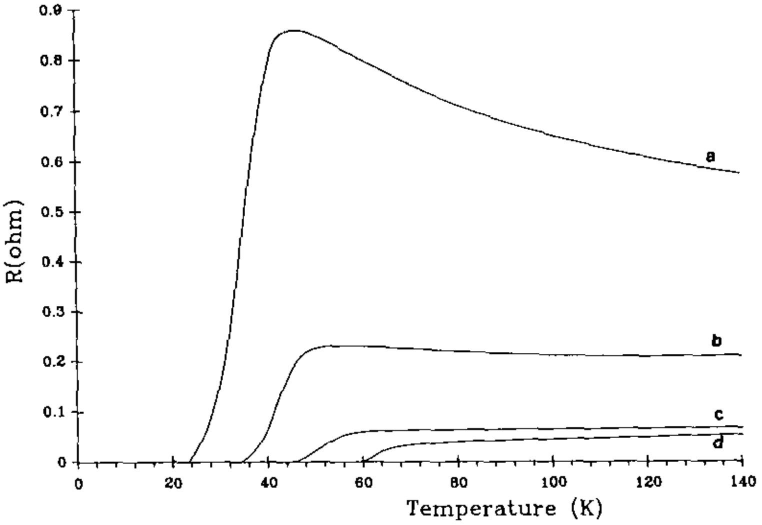

FIG. 7. Temperature dependence of the electrical resistance of $(Pb_{0.5}Cd_{0.5})Sr_2(Ca_{0.5}Y_{0.5})Cu_2O_7$ samples: a, as-synthesized at 880°C in evacuated quartz tube; b, annealed at 900°C for 10 hr in air; c, annealed at 900°C for 10 h at pO_2 = 50 bar; d, wrapped in Au foil and annealed at 970°C for 3 hr in O_2 flow.

tivity in this phase is not only optimized by a variation of oxygen stoichiometry but also by an adjustment of cadmium content, CdO being volatile at these temperatures. The fact that similar annealings applied to Cu, Mg, or Sc cuprates destroy superconductivity or decrease dramatically the superconducting volume is in agreement with this view point.

Substitution of Yb for Y: The oxides $(Pb, A)Sr_2(Yb_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$

The replacement of yttrium by ytterbium in the cadmium cuprates does not influence the superconducting properties of these materials. An oxide with the nominal composition $(Pb_{0.5}Cd_{0.5})Sr_2(Ca_{0.5}Yb_{0.5})Cu_2O_{7-\delta}$ exhibits very similar $\chi'(T)$ curves (Fig. 8) before and after annealing under the same conditions.

On the other hand, the replacement of yttrium by ytterbium in the Sc-cuprate leads to a significant improvement of superconductivity as shown for $(Pb_{0.7}Sc_{0.3})Sr_2(Ca_{0.5}Yb_{0.5})Cu_2O_{7-\delta}$ (Fig. 4), which exhibits a Tc of 50 K and a narrow transition after annealing under 20 bar for 60 hr. Similar results have been observed for "Mg–Yb" cuprates; nevertheless, the transition of the phase is broader.

Concluding Remarks

This study definitively demonstrates that various cations besides lead can be introduced in the "$Pb_{1-x}A_x$"O layers of the 1212 structure and that the nature of these cations influences the superconducting properties of these materials. Nevertheless, it is also demonstrated that the introduction of the *A* cation is not quantitative and depends strongly on the thermal treatment. In any case, it seems difficult to obtain an absolutely pure phase, owing to the great stability of the numerous other phases which can be formed in such complicated systems containing five or six different metallic elements. The broad transitions observed for these compounds can be explained by an inhomogeneous distribution of both cations and oxygen and by vacancies in the struc-

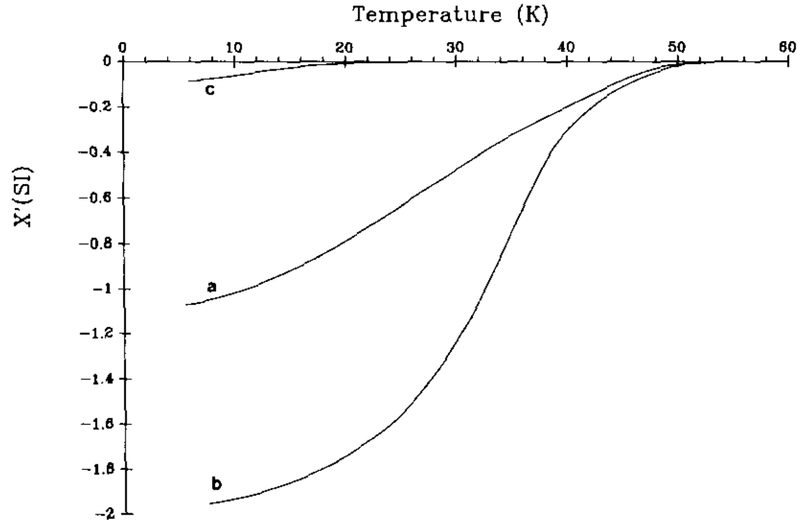

FIG. 8. AC susceptibility curves for samples of nominal composition $(Pb_{0.5}Cd_{0.5})Sr_2(Ca_{0.5}Yb_{0.5})Cu_2O_7$ annealed at 900°C for 10 hr in air (curve a) and at 970°C in gold foil for 3 hr in an O_2 flow (Curve b). Curve c corresponds to the as-synthesized sample in the evacuated quartz tube.

ture. The consideration of the maximum critical temperature of these different phases leads us to classify them into two series. The first series, with A = Cu, Mg, Zn, Sc, corresponds to critical temperatures ranging from 30 to 50 K, whereas the second series, obtained for A = Cd, Ca, Sr, exhibits Tc's ranging from 60 to 90 K. This suggests that there exists a size effect of the A cations; larger A cations might induce higher Tc's by a pressure effect, the cell volume remaining approximately constant. But the important factor is of course the oxygen stoichiometry, since, as shown here and previously, for each oxide the Tc goes through a maximum for an optimum oxygen pressure. In fact, it seems to us most probable that the oxygen content is closely related to the size of the A cations. Indeed the size of Pb(IV) is more compatible with those of small cations, such as A = Cu, Mg, Zn, Sc, whereas the introduction of larger cations such as A = Cd, Ca, Sr on the same sites should favor the formation of Pb(II). Consequently, in the cuprates corresponding to A = Cu, Mg, Zn, Sc, the formation of Pb(IV) would be favored with respect to Cu(III), so that the hole carrier density will remain low in spite of the total oxygen content tending toward "O_7." On the contrary, in the cuprates corresponding to A = Cd, Ca, Sr, a much lower oxygen content can be expected, leading to compositions close to $O_{6.7}$ as shown for "$Pb_{0.5}Sr_{0.5}$" cuprates (*2*); correlatively, in the latter oxides the mixed valency Pb(II)–Pb(IV) could possibly coexist with the mixed valency Cu(II)–Cu(III). An X-ray absorption study of these compounds should allow clarification of this issue.

References

1. T. Rouillon, J. Provost, M. Hervieu, D. Groult, C. Michel, and B. Raveau, *Physica C* **159,** 201 (1989).
2. T. Rouillon, J. Provost, M. Hervieu, D. Groult, C. Michel, and B. Raveau, *J. Solid State Chem.* **84,** 375 (1990).
3. T. Rouillon, A. Maignan, M. Hervieu, C. Michel, D. Groult, and B. Raveau, *Physica C* **171,** 7 (1990).
4. M. A. Subramanian, J. Gopalakrishnan, C. C. Torardi, P. L. Gai, E. D. Boyes, T. R. Ashew, R. B. Flippen, W. E. Farneth, and A. W. Sleight, *Physica C* **157,** 124 (1989).
5. A. Maignan, T. Rouillon, D. Groult, J. Provost, M. Hervieu, C. Michel, B. Raveau, R. S. Liu, and P. P. Edwards, *Physica C* **177,** 461 (1991).
6. X. X. Tang, D. E. Morris, and A. P. B. Sinha, *Phys. Rev. B* **43,** 7936 (1991).
7. A. One and Y. Ochida, *Jpn. J. Appl. Phys.* **29,** L586 (1990).
8. T. Maeda, K. Sakuyama, S. Koriyama, H. Yamauchi, and S. Tanaka, *Phys. Rev. B* **43,** 7866 (1991).
9. S. Adachi, H. Adachi, K. Setsune, and K. Wasa, *Jpn. J. Appl. Phys.* **30,** L690 (1991).
10. S. F. Hu, D. A. Jefferson, R. S. Liu, and P. P. Edwards, *J. Solid State Chem.* **96,** 455 (1992).
11. R. S. Liu, S. F. Hu, J. Gameson, P. P. Edwards, A. Maignan, T. Rouillon, D. Groult, and B. Raveau, *J. Solid State Chem.* **93,** 276 (1991).
12. R. S. Liu, S. F. Hu, and P. P. Edwards, *Appl. Phys. Lett.* **59,** 985 (1991).
13. R. S. Liu, D. Groult, A. Maignan, S. F. Hu, D. A. Jefferson, B. Raveau, C. Michel, M. Hervieu, and P. P. Edwards, *Physica C* **195,** 35 (1992).
14. J. Y. Lee, L. S. Swinnea, and H. Steinfink, *J. Mater. Res.* **4,** 763 (1989).
15. M. Huvé, unpublished results.
16. R. S. Liu, P. P. Edwards, Y. T. Huang, S. F. Wu, and P. T. Wu, *J. Solid State Chem.*, **86,** 334 (1990).