

Role of Isovalent Substitution of Strontium for Barium in the Superconducting Properties of Cuprates with Thallium Monolayers

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The isovalent substitution of strontium for barium in thallium monolayer cuprates is studied; three series of oxides have been isolated and characterized by X-ray diffraction: the 1201 phases $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5-\delta}$ with $0 \leq x \leq 1.20$, the 1212 phase $TlBaSrCaCu_2O_{7-\delta}$, and the 1223 phases $TlBa_{2-x}Sr_xCa_2Cu_3O_{9-\delta}$ ($0.50 \leq x \leq 1.50$). The superconducting properties of these cuprates are optimized by Ar-H₂ annealing at low temperature. It is demonstrated that, contrary to thallium bilayer cuprates, the critical temperature of these phases is not significantly affected by the Sr substitution. The 1201 cuprates are all superconducting with very similar T_c 's, close to 40 K, whatever x , i.e., equally for pure barium as for pure strontium phase. Similarly the 1212 phase $TlBaSrCaCu_2O_{7-\delta}$, with a T_c of 100 K, can be considered more interesting than $TlBa_2CaCu_2O_{7-\delta}$, which is very difficult to obtain as a perfectly pure phase. The cuprate $TlBa_{1.5}Sr_{0.5}Ca_2Cu_3O_{9-\delta}$ exhibits the highest T_c , 124 K, which has been registered up to now in the 1223 series, showing that the multiplicity of the thallium layers does not play a predominant role for superconductivity. Attention is drawn to the crucial role of the experimental conditions of annealing for the optimization of the hole carrier density.

Introduction

It is now well established that the superconducting properties of the thallium-layered cuprates are mainly governed by the copper-oxygen layers and that their critical temperature is very sensitive to small deviations from oxygen stoichiometry. Many studies have been carried out in the barium compounds, but few results have been obtained in the case of the strontium phases so that the exact role of barium and strontium in superconductivity is so far not really understood. This comes from the fact that, despite extensive efforts in different laboratories, it has often not been possible to replace completely barium by strontium and synthesize the exact Sr analogues. Nevertheless, a complete substitution has been achieved for two members of the series $Tl_2Ba_2Ca_{m-1}Cu_mO_{2m+4}$: $Tl_2Ba_{2-x}Sr_xCaCu_2O_8$ ¹ and $Tl_2Ba_{2-x}Sr_xCuO_6$,^{2,3} which correspond to $m = 2$ and 1, respectively. These studies have shown that the replacement of barium by strontium in these phases leads to a dramatic decrease of their critical temperature, since T_c is lowered to 44 K for $Tl_2Sr_2CaCu_2O_8$ ¹ and no trace of superconductivity is observed for $Tl_2Sr_2CuO_6$,^{2,3} In the case of thallium monolayer cuprates $TlBa_{2-x}Sr_xCa_{m-1}Cu_mO_{2m+3}$, a complete substitution of strontium for barium was also observed for $m = 1$ and 2 leading to the metallic phase $TlSr_2CuO_{5-\delta}$ ^{4,5} and to the superconductor $TlSr_2CaCu_2O_{7-\delta}$ ^{6,7} with a T_c of about 70

K. These results suggest that the substitution of Sr for Ba in the thallium monolayer compounds is not so dramatic as for the thallium bilayer cuprates. Indeed the 1201 phase $TlBa_2CuO_{5-\delta}$ ⁸ does not superconduct, and a T_c ranging from 50 to 110 K was observed for the 1212 phase $TlBa_2CaCu_2O_{7-\delta}$.⁸⁻¹¹ This different behavior of thallium monolayer oxides, with respect to the thallium bilayer phases, is also supported by the studies of the superconductors $TlBaSrCuO_5$,¹² $TlBaSrCaCu_2O_{7-\delta}$,¹³ and $TlBaSrCa_2Cu_3O_9$,¹⁴ which exhibit rather high T_c 's of 43, 94, and 116 K, respectively. Moreover, Subramanian et al.¹⁵ have even noted an opposite effect for the 1201 cuprates, $TlBa_{1-x}Sr_xLaCuO_{5-\delta}$, i.e., for this phase the Sr-rich ($0.7 \leq x \leq 1$) compositions are superconductors with T_c 's ranging from 37 to 44 K, whereas the Ba-rich phases are semiconductors. The recent studies of the Tl-Sr-La-Cu-O system are in agreement with these results: they show that $TlSr_{1.2}La_{0.8}CuO_{5-\delta}$ appears as the best superconductor of the 1201 family, as well by the absence of

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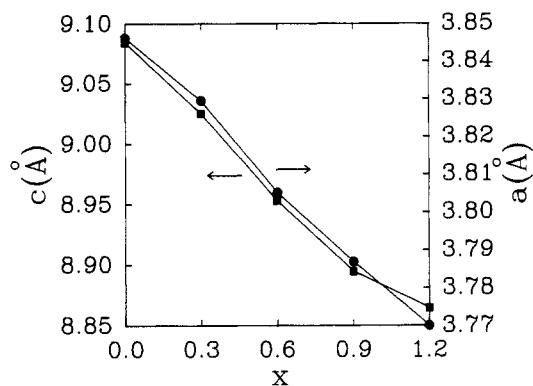


Figure 1. $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$: evolution of the cell parameters versus x .

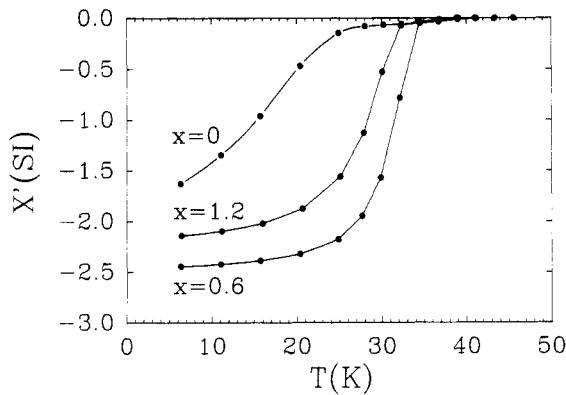


Figure 2. $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$: ac susceptibility curves χ' vs T for $x = 0, 0.6$, and 1.2 (ceramic samples) measured with $H = 0.1$ G.

intergrowth defects as by a T_c of about 40 K.¹⁶ To understand these differences, we have investigated the superconducting properties of the thallium monolayer cuprates, taking into consideration their possible optimization by annealing in a reducing atmosphere. The present paper deals with the oxides $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$, $TlBa_{2-x}Sr_xCaCu_2O_{7-\delta}$, and $TlBa_{2-x}Ca_2Cu_3O_{9-\delta}$.

Experimental Section

The oxides $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$ were prepared from Tl_2O_3 , La_2O_3 , CuO , $BaCuO_2$, $SrCuO_2$, and SrO_2 in the appropriate ratio, with the nominal composition O_6 . The samples were heated, in evacuated quartz ampule, at 930 °C for 6 h and then slowly cooled (15 °C/h). The oxides $TlBa_{2-x}Sr_xCaCu_2O_7$ were prepared by heating adequate amounts of Tl_2O_3 , BaO_2 , $SrCuO_2$, CaO , and CuO at 900 °C for 10 h in a furnace with an oxygen pressure fixed between 10 and 100 bar. The $TlBa_{2-x}Sr_xCa_2Cu_3O_9$ samples were prepared from mixtures of Tl_2O_3 , BaO_2 , $SrCuO_2$, CuO , and CaO in the appropriate ratio, in sealed quartz tubes, at 930 °C for 6 h and slowly cooled (15 °C/h).

The purity of the samples was checked by X-ray diffraction (XRD) and electron diffraction (ED). The powder X-ray diffraction patterns were registered by step scanning over an angular range of $10^\circ \leq 2\theta \leq 100^\circ$ in increment of 0.02° (2θ) by means of a Sievert diffractometer equipped with a primary monochromator ($Cu K\alpha_1$ radiation). The profile refinement computer program DBW 3.2¹⁷ was used to calculate the cell parameters and the structures.

The superconducting properties were studied by ac susceptibility and dc resistivity measurements from room temperature down to 4.2 K; no demagnetization corrections were made.

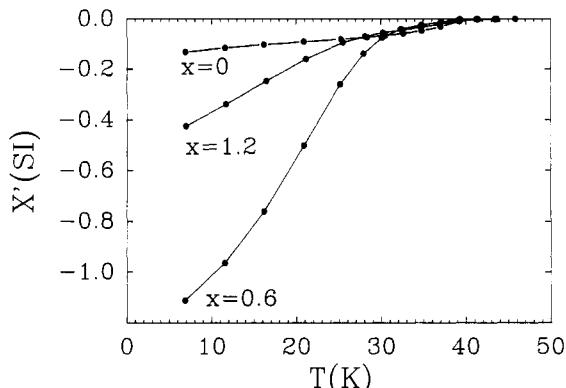


Figure 3. $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$: χ' vs T for $x = 0, 0.6$, and 1.2 (powders) measured with $H = 5$ G.

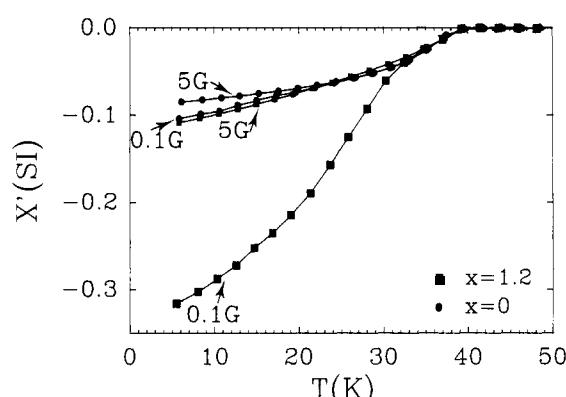


Figure 4. $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$: χ' vs T for $x = 0$ and 1.2 (powders) measured with $H = 0.1$ and 5 G.

Annealings in reducing atmosphere of Ar/H_2 have been achieved at low temperature (260 °C) in order to avoid structural damages. The purity of the annealed samples was also checked systematically ED and XRD.

Results and Discussion

For the experimental conditions described above, three series of cuprates, corresponding to $m = 1, 2$, and 3 have been synthesized as pure phases: $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$ with $0 \leq x \leq 1.2$ ($m = 1$); $TlBa_xSr_xCa_2Cu_2O_{7\pm\delta}$ ($m = 2$); $TlBa_{2-x}Sr_xCa_2Cu_3O_{9\pm\delta}$ with $0.5 \leq x \leq 1.5$ ($m = 3$).

The 1201 Oxides $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$. A complete solid solution can be isolated for $0 \leq x \leq 1.2$. The evolution of the parameters of the tetragonal cell (Figure 1) shows that both a and c decrease as x increases in agreement with the effective ionic radius of strontium, which is significantly smaller than that of barium.

The magnetic ac susceptibility curves $\chi'(T)$ of the as-synthesized pellets performed in low magnetic field (0.1 G) without any correction of the demagnetizing field are given in Figure 2 for three compositions $x = 0$, $x = 0.6$, and $x = 1.2$. One observes in all three cases large shielding volumes. The transitions range from 24 K for $x = 0$ ($Ba_{1.2}$) to 34 K for $x = 0.6$ ($Ba_{0.6}Sr_{0.6}$), a transition at 28 K being observed for the pure strontium phase ($x = 1.2$). Such transitions can be attributed to intergranular coupling since they disappear for higher field as shown from Figure 3 for $H = 5$ G. This intergranular effect is confirmed by susceptibility measurements, performed under 0.1 and 5 G, on powder specimens obtained by grinding the same pellets for $x = 0$ and $x = 1.2$ (Figure 4). Indeed one observes for both samples a superconducting volume of 10% under

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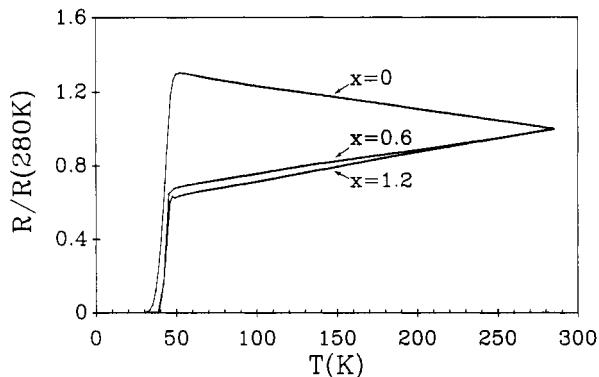


Figure 5. $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_{5\pm\delta}$: normalized resistances versus T for the three samples $x = 0, 0.6$, and 1.2 .

Table I. Atomic Coordinates Refined from Power XRD Data for Three Samples of $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_5$ ($x = 0, 0.6$, and 1.2)^a

	$TlBa_{1.2}La_{0.8}CuO_5$	$TlBa_{0.6}Sr_{0.6}La_{0.8}CuO_5$	$TlSr_{1.2}La_{0.8}CuO_5$
a (Å)	3.84619(5)	3.80510(8)	3.77011(6)
c (Å)	9.0843(1)	8.9529(2)	8.8647(1)
c/a	2.362	2.353	2.351
Tl			
x	0.086(1)	0.078(1)	0.067(1)
B (Å ²)	0.8(1)	0.2(1)	0.17(7)
Cu, Sr, La			
B (Å ²)	0.7(1)	0.5(1)	0.62(9)
B (Å ²)	0.2076(2)	0.2065(2)	0.2056(2)
B (Å ²)	0.69(5)	0.47(6)	0.28(4)
O ₁	z	0.270(2)	0.268(2)
O ₃	x	0.633(9)	0.615(9)
R_p (%)	7.22	7.17	6.45
R_{wp} (%)	9.52	10.48	9.56
R_{exp} (%)	9.51	9.59	4.29
R_i (%)	5.75	5.25	5.45

^a Space group: $P4/mmm$ with Tl in 1b (0,0,0.5) \rightarrow 4m ($x, 0, 0.5$); Cu in 1a (0,0,0); Ba, Sr, and La in 2h (0.5,0,0.2); O₁ in 2g (0,0,z); O₂ in 2f (0.5,0,0) and O₃ in 1d (0.5,0,0.5) \rightarrow 4o ($x, 0, 0.5$); the isotropic thermal factors of oxygen arbitrarily fixed at 1 Å².

Table II. Interatomic Distances (Å) for $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_5$

x	$TlBa_{1.2}La_{0.8}CuO_5$	$TlBa_{0.6}Sr_{0.6}La_{0.8}CuO_5$	$TlSr_{1.2}La_{0.8}CuO_5$
Tl-O ₁	2 2.12(1)	2.10(1)	2.05(1)
Tl-O ₃	4 2.12(2)-2.91(3)	2.17(2)-2.84(3)	2.31(2)-2.69(3)
Cu-O ₁	2 2.45(1)	2.40(2)	2.39(1)
Cu-O ₂	4 1.923(0)	1.903(0)	1.885(0)
Ba, Sr, La-O ₁	4 2.778(3)	2.747(4)	2.726(2)
Ba, Sr, La-O ₂	4 2.694(1)	2.653(1)	2.622(1)
Ba, Sr, La-O ₃	1 2.705(7)	2.664(7)	2.622(4)

5 G after grinding, whereas a weak effect subsists for $x = 1.2$ under 0.1 G.

Moreover the three samples exhibit a very similar T_c close to 40 K and a broad transition which might be due to an inhomogeneous distribution of oxygen, vacancies, and cations in the sample (Figure 3). The rather low diamagnetic volume fraction of 10%, under 5 G, might suggest an impurity effect, such as $(La, Sr)_2CuO_4$. This hypothesis has been easily ruled out by the fact that a similar compound, $TlSr_{1.2}Pr_{0.8}CuO_{5-\delta}$, was prepared with a T_c of 40 K and a similar diamagnetic volume; moreover a systematic investigation of more than 50 crystals/sample by electron diffraction did not indicate the presence of La_2CuO_4 -type phase.

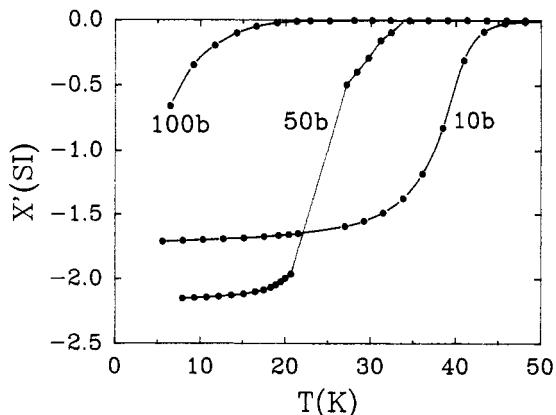


Figure 6. χ' (T) of $TlBaSrCaCu_2O_7$ synthesized under different oxygen pressures—10, 50, and 100 bar—with $H = 5$ G.

The normalized resistive curves $R(T)/R_0$ (Figure 5) are in agreement with the magnetic measurements. The T_c (onset) range from 45 to 50 K, and the T_c offsets are identical for pure strontium and “Ba/Sr” phases, close to 40 K, slightly larger than for the pure barium phase (close to 30 K). Note also that the pure barium phase ($x = 0$) exhibits a semiconducting behavior in the normal state, in agreement with the less pronounced intergranular effect observed in Figure 2.

The important result is that all the compositions of the domain are superconductive whatever x , contrary to the oxides $TlBa_{1-x}Sr_xLaCuO_{5-\delta}$ ¹⁵ for which only a small domain was found to superconduct in the strontium rich side ($0.7 \leq x \leq 1$). Moreover the superconducting volume fraction of 10%, although small, is much larger than that generally observed for all the different 1201 phases by the various authors. These results demonstrate that the model proposed by Subramanian et al.¹⁵ to explain the loss of superconductivity on the barium rich side of the 1201 structure cannot be applied here. Indeed according to this model, based on the extent of overlap between the $x^2 - y^2$ bands of $[CuO_2]_{\infty}$ and 6s band of $[TlO]_{\infty}$, a shortening of the in-plane Cu–O bonds of the CuO_6 octahedra should induce or enhance the superconducting properties.¹⁵ The similar superconducting properties of $TlBa_{1.2}La_{0.8}CuO_{5-\delta}$ and $TlSr_{1.2}La_{0.8}CuO_{5-\delta}$ despite their different a and c parameters suggest that, for this composition different of Subramanian, the length of the Cu–O bonds does not influence superconductivity dramatically. To check this view point, atomic coordinates were refined for the three compounds $x = 0, 0.6$, and 1.2 , from powder XRD data. The atomic coordinates are listed in Table I, and the interatomic distances are given in Table II. Although the oxygen positions are not very accurate, these results give a trend which can be considered as significant about the CuO_6 octahedral layers. It appears (Table II) that both the in-plane and apical Cu–O distances decrease significantly as the strontium content increases. Consequently the decrease of the in plane Cu–O distance cannot be considered as the main factor which governs superconductivity of $TlBa_{1.2-x}Sr_xLa_{0.8}CuO_5$. It is worth pointing out that different annealings under oxygen pressure or in an inert gas flow do not improve the superconducting properties of these cuprates. All attempts to increase T_c by annealing these oxides in an Ar/H_2 flow at low temperature (250–300 °C) were unsuccessful; they led to a degradation of superconductivity.

The 1212 Oxide $TlBaSrCaCu_2O_{7-\delta}$. Contrary to the 1201 structure, it has not been possible with our exper-

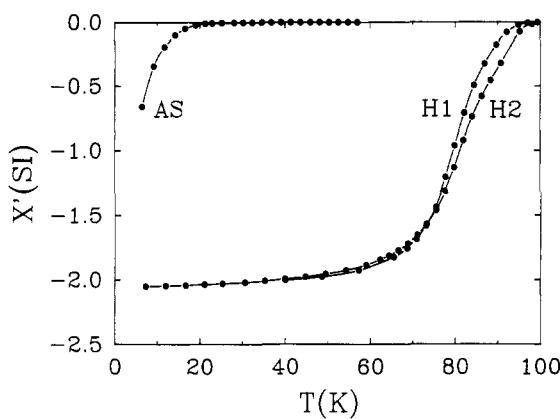


Figure 7. $\chi'(T)$, with $H = 5$ G, of as-synthesized (as) $\text{TlBaSrCaCu}_2\text{O}_7$ (100 bar of O_2) and after Ar-H_2 annealings at 290°C (plateau of 30 min (H_1) and then 1 min (H_2)).

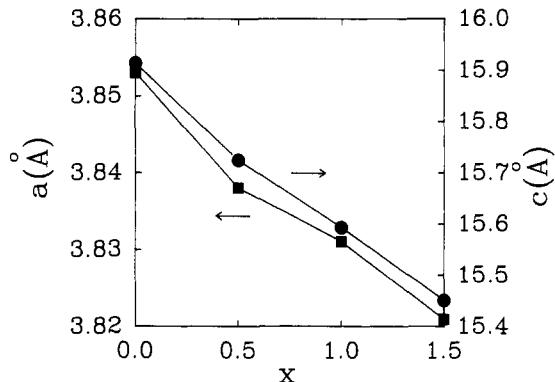


Figure 8. $\text{TlBa}_{2-x}\text{Sr}_x\text{Ca}_2\text{Cu}_3\text{O}_9$: evolution of the lattice parameters versus x .

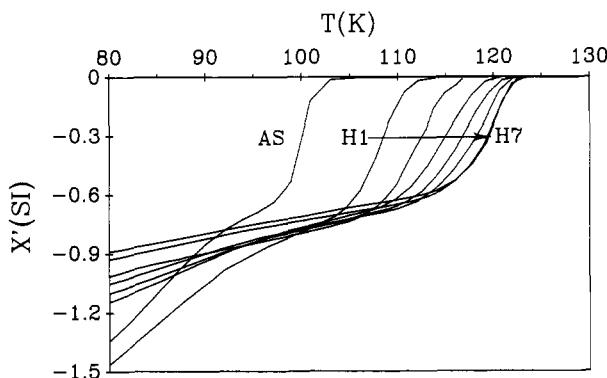


Figure 9. $\text{TlBaSrCa}_2\text{Cu}_3\text{O}_9$ ($x = 1$): $\chi'(T)$, with $H = 5$ G, for the as-synthesized sample (as) and after successive reducing annealings (H_1 to H_7).

imental conditions to prepare a solid solution $\text{TlBa}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_{7-\delta}$ with a large homogeneity range. Only one pure phase could be prepared for $x = 1$, i.e., $\text{TlBaSrCaCu}_2\text{O}_{7-\delta}$. This is in agreement with the fact that cuprates $\text{TlBa}_{2-\delta}\text{CaCu}_2\text{O}_{7-\delta}$ ⁸⁻¹¹ and $\text{TiSr}_2\text{CaCu}_2\text{O}_{7-\delta}$ ^{6,7} are difficult to synthesize as pure phases. Thus the oxide $\text{TlBaSrCaCu}_2\text{O}_{7-\delta}$ appears as the most stable phase even under high oxygen pressures.

The evolution of the ac susceptibility versus T (Figure 6) for as-synthesized samples prepared at different oxygen pressures shows that the critical temperature increases significantly as the oxygen pressure decreases: from 20 K at 100 bar to 45 K at 10 bar. The annealing of the 100-bar as-synthesized cuprate, under an argon-hydrogenated flow at low temperature, leads to a spectacular increase of the

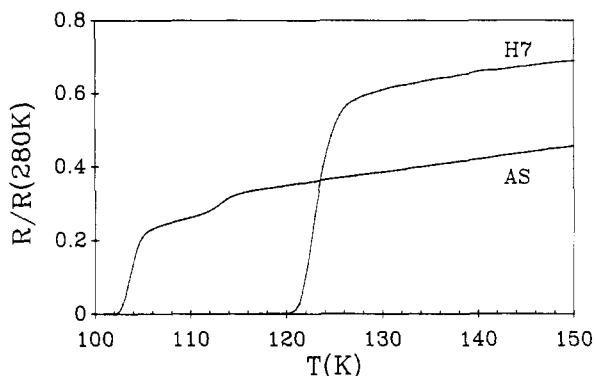


Figure 10. Normalized resistances versus T for the as-synthesized (as) sample and after seven Ar-H_2 annealings.

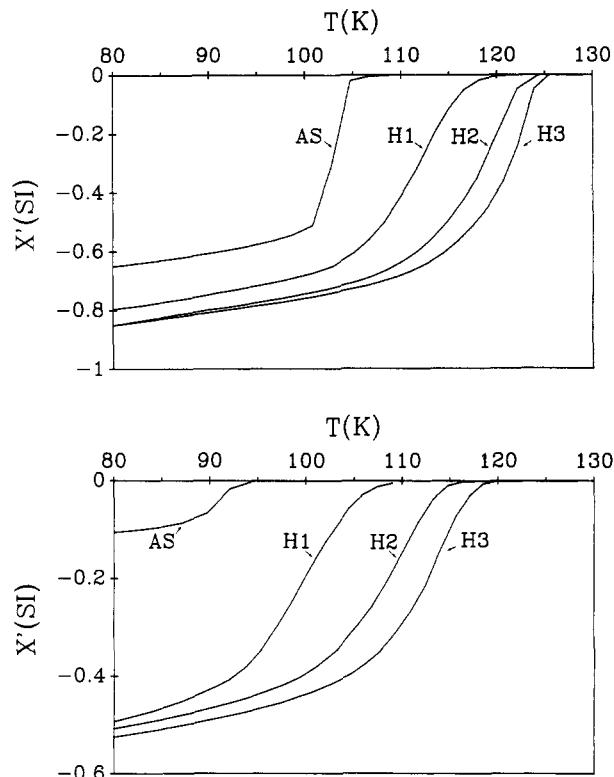


Figure 11. $\chi'(T)$, with $H = 5$ G, for the as-synthesized sample and after three successive Ar-H_2 annealings at 260°C — H_1 to H_3 —(each annealing with a plateau of 15 min): (a, top) $x = 0.5$; (b, bottom) $x = 1.5$.

critical temperature up to 100 K as shown from $\chi'(T)$ curve (Figure 7). This result is in agreement with that obtained by Gopalakrishnan et al.,¹³ who obtained for this phase a T_c of 94 K. It confirms also the important role of oxygen non stoichiometry for the optimization of T_c in thallium cuprates developed previously.^{9,18-20} Such a behavior suggests that the pure calcium phase, $\text{TlBaSrCaCu}_2\text{O}_{7-\delta}$, contains too many holes when prepared under oxygen pressure, so that the hole carrier density could be reduced even by working under 100 bar but by replacing the bivalent cation Ca^{2+} partially by a trivalent cation such as Y^{3+} . The synthesis of the superconductor $\text{TlBa-SrCa}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{7-\delta}$, under an oxygen pressure of 100 bar,

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with a T_c of 50 K (instead of 20 K for the pure calcium cuprate) confirms this view point.

The comparison of this Ar/H₂ annealed TlBaSr-CaCu₂O_{7- δ} superconductor ($T_c = 100$ K) with the nearly pure superconductor TlBa₂CaCu₂O_{7- δ} ,⁸⁻¹¹ which exhibits T_c ranging from 50 to 110 K, shows that the partial replacement of barium by strontium does not weaken the critical temperature contrary to what is observed for thallium bilayer cuprates.¹⁻³ Note also that the range of T_c 's of the TlBaSrCaCu₂O_{7- δ} phase (20–100 K) is higher than those of TlSr₂CaCu₂O_{7- δ} ,⁶ which ranges from 0 to 68 K.

The 1223 Oxides TlBa_{2-x}Sr_xCa₂Cu₃O_{9- δ} . A continuous solid solution can be isolated for $0 \leq x \leq 1.5$; all attempts to synthesize the phase TlSr₂Ca₂Cu₃O_{9- δ} ($x = 2$) were unsuccessful and always led to the formation of Sr₄Tl_{2-x}Ca_xO_{7± δ} and a Sr₁₄Cu₂₄O₄₁-type phase. The evolution of the a and c parameters of the tetragonal cell (Figure 8) shows their regular decrease as x increases, as observed for the previous series.

A previous study¹⁴ of the composition $x = 1$, i.e., TlBaSrCa₂Cu₃O_{9- δ} , showed that, after optimization under an H₂/Ar flow, the critical temperature of this phase was of 116 K, i.e., only slightly smaller than the pure barium phase TlBa₂Ca₂Cu₃O_{9- δ} which was found to be of 120 K.¹⁸ We have tried to improve the critical temperature of this phase by varying the thermal treatments under Ar/H₂ (10%) at 260 °C, using several cycles of heating up to 260 °C during 1 h without any plateau and furnace cooling. The curves $\chi'(T)$ for such a sample (Figure 9) shows that the optimization is achieved, for these conditions of temperature, for the seventh cycle with a critical temperature of 123 K, superior to that of the pure barium phase TlBa₂Ca₂Cu₃O_{9- δ} . The resistive curves for this sample (Figure 10) confirm these critical temperatures; one observes a problem of inhomogeneity for the as-synthesized sample, characterized by a hump, which disappears after H₂/Ar annealing.

A very similar behavior is observed for the $x = 0.5$ and $x = 1.5$ samples whose $\chi'(T)$ curves (Figure 11) show that the T_c is increased from 105 to 124 K and from 93 to 120 K, respectively. With this same thermal treatment, we can increase the critical temperature of the pure barium phase TlBa₂Ca₂Cu₃O_{9- δ} from 112 up to 122 K (Figure 12).

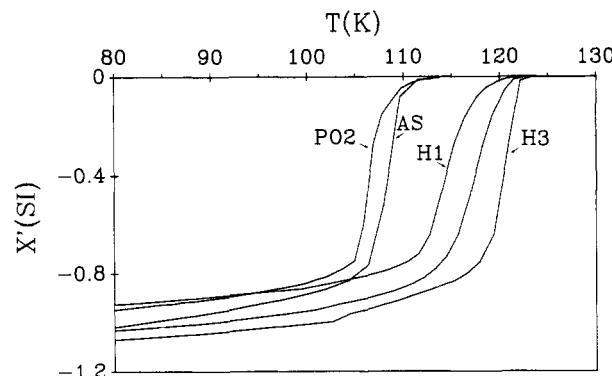


Figure 12. $\chi'(T)$, with $H = 5$ G, for TlBa₂Ca₂Cu₃O₉ ($x = 0$) as-synthesized (as); Ar-H₂ annealed (H₁–H₃) and under oxygen (100 bar) annealed (PO₂).

Note that the superconducting volume of these cuprates tends to decrease for the high strontium content ($x \sim 1.5$) especially for the as-synthesized samples.

These results demonstrate that the critical temperature of the 1223 cuprates can be increased significantly up to 124 K, i.e., close to that of the 2223 phases, by adjusting carefully the oxygen stoichiometry. But they also show that the Sr substitution does not affect dramatically the superconducting properties, the T_c 's of TlBaSrCa₂Cu₃O₉ being even slightly higher than that of TlBa₂Ca₂Cu₃O₉ after optimization in an Ar-H₂ flow.

Concluding Remarks

This study shows that the substitution of strontium for barium in the thallium monolayer cuprates 1201, 1212, and 1223 does not damage significantly the critical temperature of these phases contrary to the thallium bilayer cuprates. The comparison of the as-synthesized and Ar/H₂ annealed cuprates clearly establishes that the oxygen non-stoichiometry is the most important factor and that the conditions of annealing are very sharp for the optimization of T_c 's. In this respect the increase of T_c 's of the 1223 phase up to 124 K, very close to that of the 2223 cuprate, suggests that the “multiplicity” of the thallium layer—single or double—does not influence dramatically the critical temperature provided an adjustment of the hole carrier density, by controlling the oxygen stoichiometry, is made.