New phases in the $SrO–La_2O_3–TiO_2–CuO$ system with the K_2NiF_4 structure

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In this work some members of the $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$ and $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$ families have been synthesised in the composition ranges $0.1 \leqslant x \leqslant 1.5$ and $1.0 \leqslant x \leqslant 1.5$, respectively. A complete solid solution between La_2CuO_4 and Sr_2TiO_4, has been found by X-ray powder diffraction and no evidence of Cu/Ti ordering has been found either by these means or by electron diffraction, compositions being checked by energy dispersive analysis by X-rays (EDAX). Samples were compared before and after oxidation with BrO^- and only materials with stoichiometries close to $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$ and $La_{1.9}Sr_{0.1}Cu_{0.95}Ti_{0.05}O_{4-\delta}$ could be oxidised in these conditions. Paramagnetic susceptibilities showed the presence of small fractions of superconducting phases (T_c values close to 30 K) for samples with low titanium content ($x \leqslant 0.2$).

Materials with the K_2NiF_4 structure type, as many perovskite-related phases, are prone to substitutional chemistry, a synthesis pathway which has produced new materials, *e.g.* the first reported high-T_c superconductor, Ba-doped La_2CuO_4.[1] La^{3+} can also be substituted by Sr^{2+} instead of Ba^{2+} to give $La_{2-x}Sr_xCuO_4$ with x ranging between 0 and 1,[2] although this substitution seems to induce oxygen vacancies in the structure.[3–5] Superconductivity in La_2CuO_4, an insulator itself, is achieved by hole doping, which is associated with a formal mixed valence state of copper (Cu^{II}, Cu^{III}) within the CuO_2 layers. This hole doping has been created in many different ways, such as substitutions in the A perovskite site or intercalation of interstitial anions.[1,6–12]

Substitution on the copper site has also been explored for first-row transition metals, in order to investigate its influence on the structural and superconducting properties of $La_{1.85}Sr_{0.15}Cu_{1-y}M_yO_4$.[13–15] Ti^{IV} appears as an interesting candidate, taking into account its high charge, its tendency towards octahedral coordination and its non-magnetic d^0 configuration. On the other hand, and in the framework of the search for new superconductors, several authors have reported neutron diffraction studies of quadrupled perovskites containing copper and titanium where these cations are separated in different planes,[16–18] nevertheless, none of those materials were superconducting, maybe due to insufficient hole doping in the Cu—O layers.

Taking into account these antecedents, the strategy of this work was to explore the solid solution $La_2CuO_4–Sr_2TiO_4$ and, as a second step, to attempt to induce superconductivity by oxygen intercalation. Following these ideas, some members of the family $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$ have been synthesised in the composition range $0.1 \leqslant x \leqslant 1.5$. Although all the samples are isostructural, they can be divided into two different series: (I) we have studied the simultaneous replacement of La by Sr and Cu by Ti in La_2CuO_4 according to the general formula $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$ $(0.1 \leqslant x \leqslant 1.5)$ and achieved, for compositions close to $x=0$, evidence of superconductivity; (II) also within this range, we have varied the Sr/La ratio for a fixed 1:1 Cu:Ti ratio, according to the formula $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$, in order to learn whether the large charge and size differences between Ti^{4+} and Cu^{2+} induce a different site occupation and to explore the limits of La/Sr substitution.

Finally, in order to obtain samples as oxidized as possible and to determine the influence of oxidation on the structure and magnetic properties, chemical oxidation at room temperature was performed following the procedure described by Schöllhorn and Rudolf[9] for La_2CuO_4.

Experimental

Members of the family $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$ were synthesised from high-purity (>99.9%) La_2O_3, $SrCO_3$, CuO and TiO_2 (anatase). After decomposition of the carbonate, the powder was pressed to pellets (9 bar, diameter 11 mm), and heated for 48 h in air at 1120–1260 °C, depending on the copper content. Then, the pellets were reground and the phase homogeneity was examined by X-ray powder diffraction, using a Siemens D5000 diffractometer with Ni-filtered Cu-Kα radiation. This procedure was repeated until the pattern did not change. Rietveld analysis of the data and structural characterization were performed using the program Fullprof.[19]

Chemical oxidation of the above-mentioned compounds was performed using the following procedure: the starting material was stirred for 24 h at room temperature in a sodium hypobromite solution, prepared by addition of 3 ml of Br_2 to 100 ml of a 5 mol dm^{-3} NaOH aqueous solution at 0 °C. After this reaction the product was filtered, washed several times with water and acetone, and finally dried in vacuum. The redox process taking place can be described by the following reaction:

$$La_{2-x}Sr_x\{Cu^{II}{}_{1-z}Cu^{III}{}_z\}_{1-x/2}Ti_{x/2}O_{4+z/2}+a\ BrO^- \rightarrow$$

$$La_{2-x}Sr_x\{Cu^{II}{}_{1-z-2a}Cu^{III}{}_{z+2a}\}_{1-x/2}Ti_{x/2}O_{(4+z/2)+a}+a\ Br^-$$

The temperature dependence of the magnetic susceptibility χ was measured for powder samples using a DMS-500 magnetometer (temperature range 290–77 K, applied field 12 000 G). Selected samples were measured between 4 and 300 K with a SQUID magnetometer (Quantum Design, applied field 50 G). All samples were also tested for superconductivity by measuring the magnetic moment at 5 K. For those showing superconducting behaviour, the magnetic susceptibility *vs.* temperature was measured up to the transition temperature.

Samples for transmission electron microscopy were crushed in an agate mortar and ground in *n*-butyl alcohol; drops of the suspension obtained were deposited on a carbon-coated copper grid. Electron diffraction was carried out using a JEOL 2000 FX microscope working at 200 kV. Usually between 10 and 15 crystals of the same compound were studied.

EDAX and SEM analyses were performed with a JEOL JSM 6400 scanning microscope equipped with a Link Pentafet EDX (Model 6569) element analysis system. The specimens were prepared by grinding the powder sample, dispersing it in *n*-butyl alcohol, and depositing a droplet of this suspension onto a carbon sample holder. Afterwards a thin gold film was evaporated onto the sample.

Results and Discussion

The $La_{2-x}Sr_xCu_{1-y}Ti_yO_{4-\delta}$ system

Structural features. Fig. 1 shows, as an example, the X-ray powder diffraction pattern of $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$. A tiny amount of an unknown phase is present in this particular material, which is the least pure of the samples prepared. In all cases the diffraction peaks could be indexed according to the K_2NiF_4 structure type.[20] As can be seen from the data in Fig. 2(*a*) and (*b*), the lattice constant ***c*** increases monotonically with increasing copper and lanthanum content until the composition $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$ is reached, while a slight decrease of the ***a*** parameter can be observed; therefore the ***c/a*** ratio increases. In the composition range between $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$ and La_2CuO_4 the lattice parameters are nearly constant. Concerning the solid solution, slight deviations from Vegard's law are found: positive in the ***c*** values and negative in the ***a*** parameter.

To interpret these results, several combined effects have to be considered: ionic radii, Jahn–Teller and electronic features. Regarding the Cu^{2+} for Ti^{4+} substitution, the ionic radius of six-coordinate Cu^{2+} (0.73 Å) is greater than that of Ti^{4+} (0.605 Å)[21] leading to an increase in the cell parameters. Regarding the La^{3+} for Sr^{2+} substitution, the effect is opposite [ionic radii (CN 9): Sr^{2+} 1.31 Å, La^{3+} 1.20 Å] and greater (because of the stoichiometry) and should lead to a decrease in the ***c*** axis, as documented for instance in the system $La_{2-x}Sr_xCuO_4$.[22,23] Thus, and taking into account only steric effects, a slight decrease in the ***a*** and ***c*** cell parameters should be observed. On the other hand, the Jahn–Teller effect of Cu^{2+} accounts for the observed enlargement of the ***c*** axis parameter. An electronic effect also occurs: Cu^{2+} ions have, in an octahedral environment (contrary to Ti^{4+}), an electron in the antibonding x^2-y^2 orbital which increases the ***a*** axis parameter. This argumentation is valid in the composition range between Sr_2TiO_4 and $La_{1.7}Sr_{0.5}Cu_{0.85}Ti_{0.15}O_{4-\delta}$.

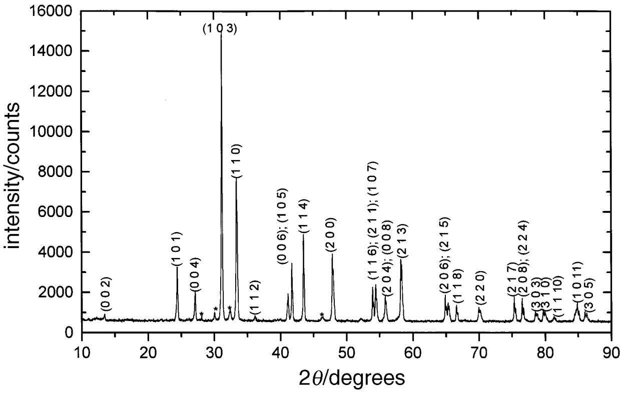

Fig. 1 X-Ray powder diffraction pattern of $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$; *, unknown phase

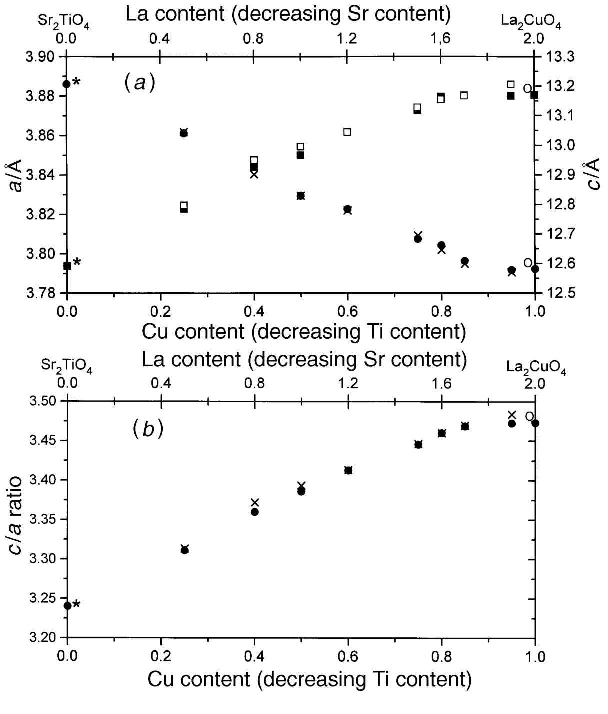

Fig. 2 (*a*) Lattice constants *a* and *c vs.* composition of several compounds of the system $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$. Data marked with * are from ref. 14 and those marked with ○ from ref. 15. ● = *a* air-prepared samples; ■ = *c* air-prepared samples; × = *a* oxidised samples; □ = *c* oxidised samples. (*b*) *c/a vs.* composition of some samples of the system $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$. Symbols and references as in (*a*).

In the composition range between $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$ and La_2CuO_4 the lattice parameter ***c*** and the ***c/a*** ratio are nearly constant. This can be interpreted on the basis of the formation of Cu^{3+} in this composition range (see below) because low-spin Cu^{3+} does not show a Jahn–Teller effect. Also, in this region of the solid solution no differences in the ***a*** parameter are detectable, which is not easy to understand as, besides other effects, for higher amounts of Cu^{3+} the electronic effect discussed above diminishes and ***a*** should decrease. A last factor, the oxygen stoichiometry, which was not examined in this work, could be responsible for this behaviour, as it is well known for this structure to admit some interstitial oxygen. Further work on neutron diffraction is in progress to examine this part of the solid solution.

EDAX and EM analysis. Fig. 3(*a*) shows, as an example, a scanning electron micrograph of a 240 μm × 170 μm area of an $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ sample and, in Fig. 3(*b*), a particle of this material can be seen. The sample appears homogeneous and shows the typical plate-like morphology of a K_2NiF_4-type compound. Together with these SEM observations, elemental analysis for different crystals has been performed by EDAX and, in Table 1, the nominal compositions (starting materials) of a few samples and those obtained by EDAX are compared. Although the detected amount of titanium is always slightly higher than the nominal composition, it should be noted that the analysis of titanium in the presence of lanthanum is difficult, because of the overlapping of the absorption peaks K of titanium and L of lanthanum. On the other hand, the results obtained by this technique depend on the sample surface roughness, proper accuracy being obtained on flat, polished samples, which is not the case here. Nevertheless, taking into account experimental errors, the results seem to indicate that the materials are homogeneous and close to the nominal composition.

Electron diffraction study. The X-ray powder structure determination did not indicate the occurrence of superstructures. Electron diffraction studies were performed and Fig. 4(*a*)–(*c*) show some diffraction patterns of the sample $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ before [Fig. 4(*a*) and (*b*)] and after [Fig. 4(*c*)] the oxidation process.

Other samples of this series were also investigated. All samples showed similar diffraction patterns and lattice constants in good agreement with those determined by X-ray powder diffraction. All these patterns can be indexed with a tetragonal centred cell and no evidence of superstructures or an ordering of the cations could be found. Moreover, even short-range ordering does not seem to exist as diffuse scattering is never observed; *i.e.* copper and titanium are distributed randomly.

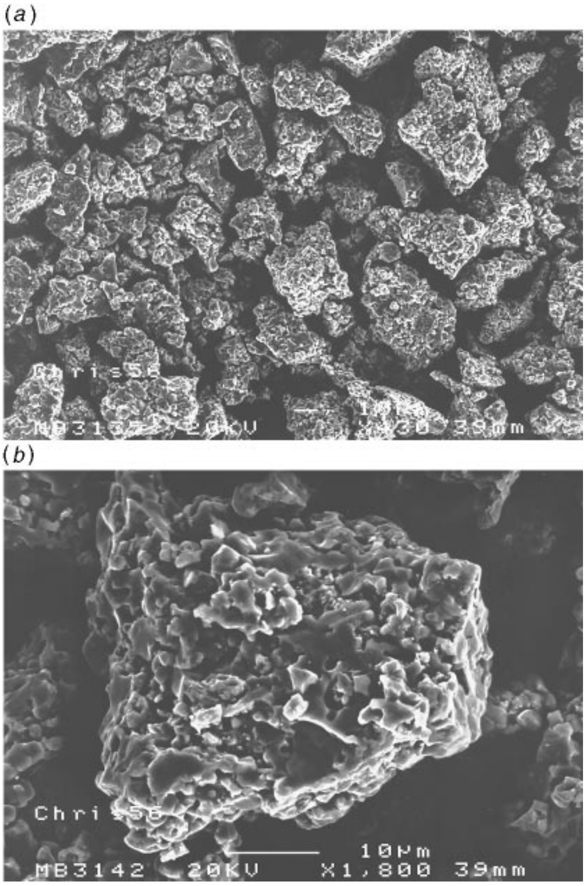

Fig. 3 Micrographs of (*a*) a 240 μm × 170 μm area of $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$, average composition: $La_{1.57}Sr_{0.36}Cu_{0.8}Ti_{0.24}O_{4-\delta}$; (*b*) a particle of $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$, average composition: $La_{1.57}Sr_{0.36}Cu_{0.8}Ti_{0.24}O_{4-\delta}$

Table 1 Relation between the nominal and detected compositions of the compounds of the series $La_{2-x}Sr_xCu_{1-y}Ti_yO_{4-\delta}$

nominal composition	detected composition
$La_{0.5}Sr_{1.5}Cu_{0.25}Ti_{0.75}O_{4-\delta}$	$La_{0.53}Sr_{1.43}Cu_{0.23}Ti_{0.76}O_{4-\delta}$
$LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$	$La_{0.9}Sr_{0.8}Cu_{0.51}Ti_{0.5}O_{4-\delta}$
$La_{1.5}Sr_{0.5}Cu_{0.75}Ti_{0.25}O_{4-\delta}$	$La_{1.52}Sr_{0.46}Cu_{0.73}Ti_{0.27}O_{4-\delta}$
$La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$	$La_{1.57}Sr_{0.36}Cu_{0.80}Ti_{0.23}O_{4-\delta}$
$La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$	$La_{1.7}Sr_{0.27}Cu_{0.83}Ti_{0.16}O_{4-\delta}$
$La_{1.9}Sr_{0.1}Cu_{0.95}Ti_{0.05}O_{4-\delta}$	$La_{1.88}Sr_{0.11}Cu_{0.94}Ti_{0.05}O_{4-\delta}$

Chemical oxidation of $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$. As can be seen from the data of Fig. 2 the oxidised compounds show the same trend as the starting materials and only the compounds near stoichiometric compositions show a slight difference in the ***c*** lattice parameters and in the ***c***/***a*** ratio. This could be due to the insertion of extra oxygen in an interstitial site as described in the literature for La_2CuO_4.[24] However, from the change of the lattice constants only, it is not evident that, for these materials, an oxidation process has taken place.

Magnetic measurements of $La_{2-x}Sr_xCu_{1-x/2}Ti_{x/2}O_{4-\delta}$. Table 2 summarises the magnetic data, the Curie temperature and the calculated values taking into account the spin-only approximation $[\mu_t = \sqrt{2S(S+1)}]$.[25] Also, as some of these materials were found to be superconductors, their transition temperatures are listed. As an example Fig. 5 shows the χ^{-1} *vs. T* plots of four different compounds. It can be seen that they obey a Curie–Weiss law.

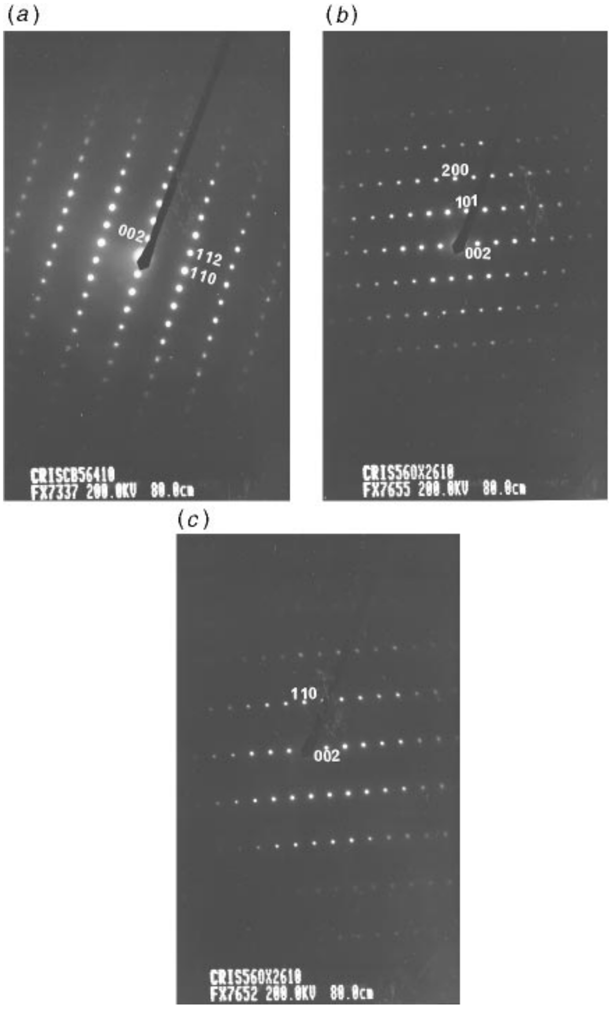

Fig. 4 Electron diffraction patterns of (*a*) a crystal of $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ (zone axis [1 1 0]); (*b*) a crystal of $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ along the [0 0 1] zone axis; (*c*) a crystal of $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ treated for 24 h in a hypobromite solution. The pattern shows the [1 1 0] orientation.

Table 2 Compositions, experimental (μ_{eff}) and theoretical (μ_t) values of the magnetic moment, Curie temperatures (θ_C) and transition temperatures (T_C) of the compounds of the series $La_{2-x}Sr_xCu_{1-y}Ti_yO_{4-\delta}$

composition	μ_{eff}/μ_B	μ_t/μ_B	θ_C/K	T_C/K
$La_{0.5}Sr_{1.5}Cu_{0.25}Ti_{0.75}O_{4-\delta}$	0.46	0.43	−13	
$La_{0.5}Sr_{1.5}Cu_{0.25}Ti_{0.75}O_{4-\delta}{}^a$	0.46	0.43	−15	
$La_{0.8}Sr_{1.2}Cu_{0.4}Ti_{0.6}O_{4-\delta}$	0.71	0.69	−21	
$La_{0.8}Sr_{1.2}Cu_{0.4}Ti_{0.6}O_{4-\delta}{}^a$	0.70	0.69	−19	
$LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$	0.87	0.87	−18	
$LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}{}^a$	0.62	0.87	−20	
$La_{1.2}Sr_{0.8}Cu_{0.6}Ti_{0.4}O_{4-\delta}$	1.06	1.04	−2	
$La_{1.2}Sr_{0.8}Cu_{0.6}Ti_{0.4}O_{4-\delta}{}^a$	1.05	1.04	−4	
$La_{1.5}Sr_{0.5}Cu_{0.75}Ti_{0.25}O_{4-\delta}$	1.28	1.30	−5	
$La_{1.5}Sr_{0.5}Cu_{0.75}Ti_{0.25}O_{4-\delta}{}^a$	1.29	1.30	−8	
$La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$	0.46	1.39		27
$La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}{}^a$	0.45	1.39		33
$La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$	0.27	1.47		25
$La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}{}^a$	0.20	1.47		23
$La_{1.9}Sr_{0.1}Cu_{0.95}Ti_{0.05}O_{4-\delta}$	0.33	1.65	−12	
$La_{1.9}Sr_{0.1}Cu_{0.95}Ti_{0.05}O_{4-\delta}{}^a$	0.32	1.65		33

[a] Treated for 24 h in a solution of 5 mol dm^{-3} NaOH with Br_2.

From the data in Table 2 it can also be seen that, in the composition range Sr_2TiO_4 to $La_{1.6}Sr_{0.4}Cu_{0.75}Ti_{0.25}O_{4-\delta}$, the experimental and calculated values are in good agreement even for the 'oxidised' samples. Only for the compound $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$ can a slight difference for the oxidised sample be detected. This indicates that the magnetic behaviour of these materials is dominated by the presence of Cu^{2+} ions, and only for the $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$ compound has a slight oxidation process taken place (see also the previous section).

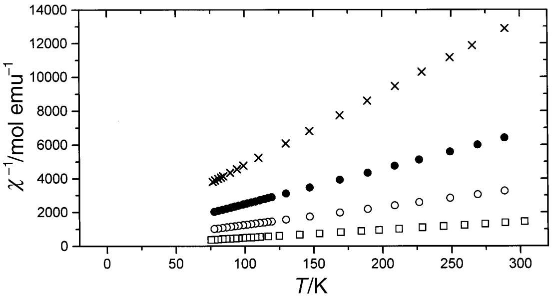

Fig. 5 Inverse susceptibility *vs.* temperature of: × = $La_{0.5}Sr_{1.5}Cu_{0.25}Ti_{0.75}O_{4-\delta}$; ○ = $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$; □ = $La_{1.5}Sr_{0.5}Cu_{0.75}Ti_{0.25}O_{4-\delta}$; ● = $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$ (24 h in 5 mol dm^{-3} NaOH/Br$_2$)

On the other hand, in the composition range between $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_4$ and La_2CuO_4, the difference between the experimental and theoretical values is evident. Fig. 6 shows the magnetic behaviour of these compounds in the temperature range 77–280 K as a plot of χ^{-1} *vs.* *T*. All samples show a very low magnetic moment which could be explained by the presence of Cu^{3+} ions, as described previously in relation to the structural features. It can be observed that the Cu^{3+} ion content reaches a maximum for the sample $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$ as this is the only compound which shows a different μ_{eff} after the oxidising process.

For compositions close to La_2CuO_4 evidence of superconductivity has been found and Fig. 7(*a*) shows, as an example, two curves of χ *vs.* *T* for $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$ and $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$. The transition is very broad and the superconducting phase corresponds in this case to 0.5–2% of the ideal $1/4\pi$ diamagnetism. As the superconducting fraction is so small, beyond the limits of XRD detection of crystalline impurities, an important question is whether or not superconductivity is really due to the titanium-containing material. From the data in Table 2 it can be remarked that there is no general trend between the titanium content and T_c. However, it can be observed that, with increasing titanium content the transition is broadened. It seems then that titanium hinders the transition.

On the other hand, for samples in the above-mentioned composition range the oxidised samples show higher transition temperatures than the non-oxidised compounds. Fig. 7(*b*) shows the χ *vs.* *T* curves for the $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ compound. This behaviour is similar to that well known in La_2CuO_4 where superconductivity is achieved by oxygen intercalation in the (1/4, 1/4, 1/4) interstitial site.[24,26,27] Neutron diffraction studies are in progress to confirm the presence of interstitial oxygen in the titanium-doped samples.

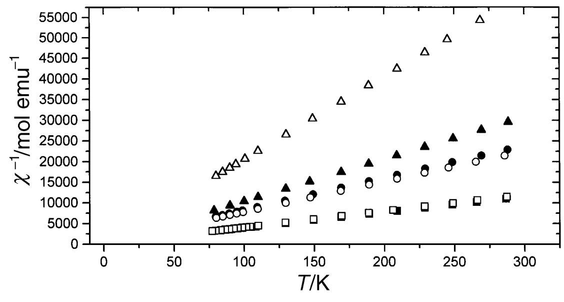

Fig. 6 Inverse susceptibility *vs.* temperature of: ■ = $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$; □ = $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ (24 h in 5 mol dm^{-3} NaOH/Br$_2$); ▲ = $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$; △ = $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$ (24 h in 5 mol dm^{-3} NaOH/Br$_2$); ● = $La_{1.9}Sr_{0.1}Cu_{0.95}Ti_{0.05}O_{4-\delta}$; ○ = $La_{1.9}Sr_{0.1}Cu_{0.95}Ti_{0.05}O_{4-\delta}$ (24 h in 5 mol dm^{-3} NaOH/Br$_2$)

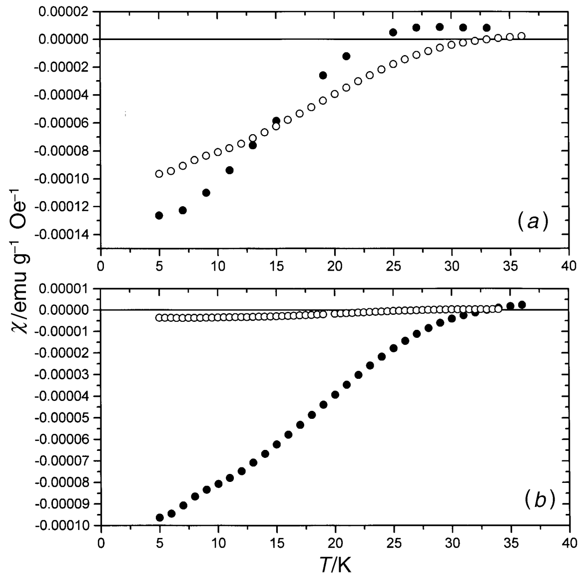

Fig. 7 Susceptibility *vs.* temperature of: (*a*) ● = $La_{1.7}Sr_{0.3}Cu_{0.85}Ti_{0.15}O_{4-\delta}$ (24 h in 5 mol dm^{-3} NaOH/Br$_2$); ○ = $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ (24 h in 5 mol dm^{-3} NaOH/Br$_2$); (*b*) ○ = $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ (air-prepared); ● = $La_{1.6}Sr_{0.4}Cu_{0.8}Ti_{0.2}O_{4-\delta}$ (24 h in 5 mol dm^{-3} NaOH/Br$_2$)

The $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$

Structural features. Samples with $1 \leqslant x \leqslant 1.5$ were prepared as described above. Fig. 8(*a*) and (*b*) show the lattice parameters. As can be seen from these data, the materials show a general trend: ***a*** increases and the long parameter ***c*** decreases with increasing Sr content. As a consequence, the ***c/a*** ratio decreases as the Sr content increases. Note that this behaviour is opposite to that observed for the La/Sr substitution in La_2CuO_4.

As it is well known in La_2CuO_4 the oxidation of the CuO_2 layers (hole doping) removes electrons from the $d_{x^2-y^2}$ bands[28] which have antibonding character in the in-plane Cu—O bonds. As the number of holes increases, the in-plane Cu—O bond length (d_{Cu-O}) is shortened. In addition to this electronic factor, the in-plane d_{Cu-O} is also controlled by a non-electronic factor

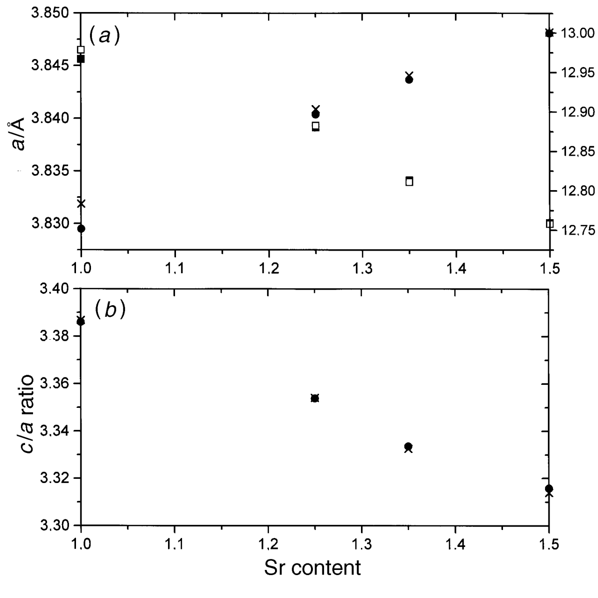

Fig. 8 (*a*) Lattice constants *a* and *c* *vs.* Sr content for several compounds of the system $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$: ● = *a* air-prepared samples; ■ = *c* air-prepared samples; × = *a* oxidised samples; □ = *c* oxidised samples. (*b*) *c*/*a* ratio *vs.* Sr content for several compounds of the system $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$ Symbols as in (*a*).

(for example, steric strain)[29] associated with the cations located at the nine-coordinate sites adjacent to the CuO_2 layers. With the increasing size of the nine-coordinate site cations [ionic radii (CN 9): Sr^{2+} 1.31 Å, La^{3+} 1.20 Å],[21] the in-plane Cu—O bond is lengthened to reduce the resulting steric strain. It seems then, that in this series the steric factor has a greater influence on the ***a*** lattice parameter than does the electronic factor. This is indeed related to the relatively high amount of titanium for which the electronic factor is obviously negligible. The decrease in the ***c*** axis parameter is more difficult to explain, since as stated above, Sr^{2+} is bigger than La^{3+}. Nevertheless, it is related to two effects: (I) hole doping leads to an increase of the Cu^{3+} content and to a reduction of the Jahn–Teller effect. This would shorten the Cu—O distance along the ***c*** axis; and (II) it is also probable that a higher Sr content leads to oxygen vacancies in these samples, especially for $La_{0.5}Sr_{1.5}Cu_{0.5}Ti_{0.5}O_{4-\delta}$, in which all copper would be Cu^{3+} if the sample had its full theoretical oxygen content. This would produce some lattice relaxation and consequently an increase in ***c***.

Table 3 Atomic positions, temperature factors *B*, occupation numbers *n*, lattice constants and residuals for the integrated intensities, profile, weighted, expected and the 'goodness of fit' χ^2 obtained for $La_{0.65}Sr_{1.35}Ti_{0.5}Cu_{0.5}O_{4-\delta}$ with the space group *I*4/*mmm*

atom	site	*x*	*y*	*z*	*B*/Å^2	*n*
Sr	4e	0	0	0.356(1)	0.2(1)	0.67(5)
La	4e	0	0	0.356(1)	0.2(1)	0.32(5)
Ti	2a	0	0	0	0.2(1)	0.58(2)
Cu	2a	0	0	0	0.1(1)	0.42(2)
O(1)	4c	0.5	0	0	0.8(1)	0.9(1)
O(2)	4e	0	0	0.162(5)	0.6(1)	1.00

$a=3.8434(6)$ Å; $c=12.811(2)$ Å; $V=189.2(5)$ Å^3. $R_B=4.52\%$, $R_p=5.80\%$, $R_{wp}=7.25\%$, $R_{ex}=4.23\%$, χ^2 (GOF)$=2.94$.

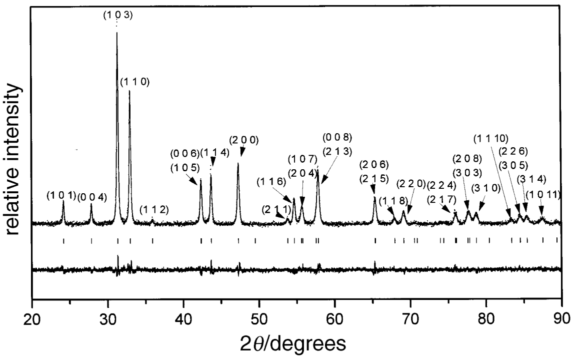

Fig. 9 Profile analysis of an XRD pattern of $La_{0.65}Sr_{1.35}Cu_{0.5}Ti_{0.5}O_{4-\delta}$. The set of tick marks below the data indicate the position of the allowed reflections. The lower trace represents the difference between the observed and calculated profiles (see also Tables 2 and 3).

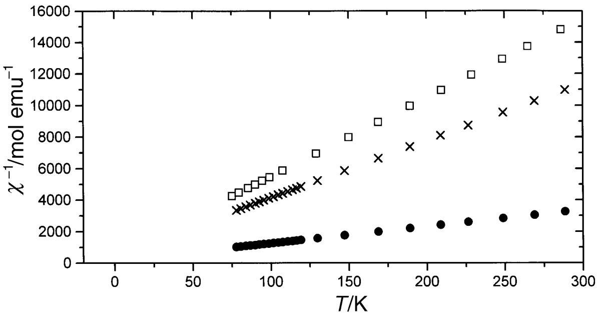

Fig. 10 Inverse susceptibility *vs.* temperature of: ● = $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$; □ = $La_{0.75}Sr_{1.25}Cu_{0.5}Ti_{0.5}O_{4-\delta}$; × = $La_{0.5}Sr_{1.5}Cu_{0.5}Ti_{0.5}O_{4-\delta}$

It then seems that the first factor is somewhat predominant in this series of samples, since the number of vacancies, although noticeable (see below), is not very high.

A Rietveld structural refinement for $La_{0.65}Sr_{1.35}Cu_{0.5}Ti_{0.5}O_{4-\delta}$ seems to indicate that the structure indeed has vacancies [see Table 3: occupation factor O(1)= 0.9] in the 4c oxygen sites of the K_2NiF_4-like structure.[19,30] Fig. 9 shows the experimental and difference diffraction patterns and Table 3 gives the structural data. These data do not show an ordering of the Ti^{4+}/Cu^{2+} cations on the B sites or of La^{3+}/Sr^{2+} on the A sites. Neutron diffraction data are necessary to fully elucidate this structure.

Chemical oxidation of $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$. The lattice parameters of the oxidised samples are summarised in Fig. 8(*a*) and (*b*). As can be seen from these data and with the exception of the stoichiometric compound, namely $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$, no significant changes in the lattice parameters are observed upon oxidation. This could be explained taking into account that for higher strontium contents in the non-oxidised compounds, the Cu^{3+} content should increase unless oxygen vacancies appear. Obviously, the higher the oxidation state of copper, the more difficult it is to achieve further oxidation.

Magnetic measurements of $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$. Table 4 summarises the experimental and calculated data as obtained with the spin-only approximation. From these data it can be seen that, only for the first member of this series, namely $LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$, are the experimental and the calculated values in good agreement. For the remaining samples, the experimental data are nearly one half of the expected values. This could be explained by a higher amount of Cu^{3+} ions in these materials. Cu^{3+} in a d^8 and low-spin configuration is a diamagnetic ion. Consequently, with increasing Cu^{3+} content the magnetic moment decreases in these materials.

It can also be seen that the Cu^{2+}/Cu^{3+} ratio does not differ for the last three compounds. Taking into account the normal oxidation states of La^{3+}, Sr^{2+} and Ti^{4+}, it follows that, in the last two members of the series, namely $La_{0.65}Sr_{1.35}Cu_{0.5}Ti_{0.5}O_{4-\delta}$ and $La_{0.5}Sr_{1.5}Cu_{0.5}Ti_{0.5}O_{4-\delta}$, oxygen vacancies seem to be present. With a decreasing amount of oxygen and an increasing amount of strontium the

Table 4 Experimental magnetic moments, theoretical values, Curie temperatures θ_C and Cu^{2+}/Cu^{3+} ratios of compounds of the series $La_{2-x}Sr_xCu_{0.5}Ti_{0.5}O_{4-\delta}$

composition	μ_{eff}/μ_B	μ_t/μ_B	θ_C/K	Cu^{2+}/Cu^{3+} (%)
$LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$	0.87	0.87	−18	100:0
$LaSrCu_{0.5}Ti_{0.5}O_{4-\delta}$[a]	0.62	0.87	−19	71:29
$La_{0.75}Sr_{1.25}Cu_{0.5}Ti_{0.5}O_{4-\delta}$	0.39	0.87	−10	44:56
$La_{0.75}Sr_{1.25}Cu_{0.5}Ti_{0.5}O_{4-\delta}$[a]	0.40	0.87	−11	46:54
$La_{0.65}Sr_{1.35}Cu_{0.5}Ti_{0.5}O_{4-\delta}$	0.43	0.87	−17	49:51
$La_{0.65}Sr_{1.35}Cu_{0.5}Ti_{0.5}O_{4-\delta}$[a]	0.43	0.87	−17	49:51
$La_{0.5}Sr_{1.5}Cu_{0.5}Ti_{0.5}O_{4-\delta}$	0.47	0.87	−15	54:46
$La_{0.5}Sr_{1.5}Cu_{0.5}Ti_{0.5}O_{4-\delta}$[a]	0.49	0.87	−15	56:44

[a] Treated for 24 h in a solution of 5 mol dm^{-3} NaOH with Br_2.

Cu^{2+}/Cu^{3+} ratio is constant. Rietveld refinements have indeed shown oxygen vacancies as described above.

Fig. 10 gives, as an example, the resulting χ^{-1} *vs.* T curves of three compounds. It can be seen that the materials obey a Curie–Weiss behaviour. None of the samples show a transition to the superconducting state down to 5 K.

We thank the European Community for grants given to C. S. (EEC Network programs CHRX-CT93-0116 and CHRX-CT94-0461) and the Spanish CICYT (MAT-92-0374 and MAT95-0809) for financial support. The technical assistance from the Centro de Microscopía Electrónica, UCM, is also appreciated.

References

1 J. G. Bednorz and K. A. Müller, *Z. Phys. B*, 1986, **64**, 189.
2 N. Nguyen, J. Choisnet, M. Hervieu and B. Raveau, *J. Solid State Chem.*, 1981, **39**, 120.
3 J. B. Torrance, Y. Tokura, A. J. Nazzal, A. Bezinge, T. C. Huang and S. S. P. Parkin, *Phys. Rev. Lett.*, 1988, **61**, 1127.
4 T. Kamiyama, F. Izumi, H. Asano, H. Takagi, S. Uchida, Y. Tokura, E. Takayama, M. Matsuda, K. Yamada, Y. Endoh and Y. Hidaka, *Physica C*, 1990, **172**, 120.
5 R. Yoshizaki, N. Kuroda, S. Nakamura and N. Ishikawa, *Physica C*, 1992, **199**, 143.
6 D. C. Johnston, J. P. Stokes, D. P. Goshorn and J. T. Lewandowski, *Phys. Rev. B*, 1987, **36**, 4007.
7 G. Demazeau, F. Tresse, T. Plante, B. Chevalier, J. Etourneau, C. Michel, M. Hervieu, B. Raveau, B. Lejay, A. Sulpice and R. Tournier, *Physica C*, 1988, **153**, 121.
8 E. Schirber, B. Morosin, R. M. Merill, P. F. Hlava, E. L. Venturini, J. F. Kubak, P. J. Nigrey, R. J. Baughman and D. S. Ginley, *Physica C*, 1988, **152**, 121.
9 R. Schöllhorn and P. Rudolf, *J. Chem. Soc., Chem. Commun.*, 1992, 1158.
10 A. Wattiaux, J. C. Park, J. C. Grenier and M. Pouchard, *C.R. Acad. Sci. Paris, Ser. 2*, 1990, **310**, 1047.
11 B. G. Bagley, L. H. Greene, J. M. Tarascon and G. W. Hull, *Appl. Phys. Lett.*, 1987, **51**, 622.
12 B. Chevalier, A. Tressaud, B. Lépine, K. Amine, J. M. Dance, L. Lozano, E. Hickey and J. Etourneau, *Physica C*, 1990, **167**, 97.
13 J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner and E. J. McNiff Jr. *Phys. Rev. B*, 1987, **36**, 8393.
14 G. Xiao, A. Bakhshai, M. Z. Cieplak, Z. Tesanovic and C. L. Chien, *Phys. Rev. B*, 1989, **39**, 315.
15 E. Wang, J. M. Tarascon, L. H. Greene, G. W. Hull and W. R. McKinnon, *Phys. Rev. B*, 1990, **41**, 6582.
16 P. Gómez-Romero, M. R. Palacín and J. Rodríguez-Carvajal, *Chem. Mater.*, 1994, **6**, 2118.
17 M. R. Palacín, A. Fuertes, N. Casañ-Pastor and P. Gómez-Romero, *Adv. Mater*, 1994, **6**, 54.
18 A. Gomerzano and M. T. Weller, *Chem. Mater.*, 1995, **7**, 1625.
19 J. Rodríguez-Carvajal, Fullprof program, ILL, Grenoble, 1990.
20 R. N. Ruddlesden and P. Popper, *Acta Crystallogr.*, 1957, **10**, 538.
21 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
22 C. Rial, E. Morán and M. A. Alario-Franco, *J. Supercond.*, 1994, **7**, 913.
23 M. A. Señaris Rodriguez, Doctoral Thesis, University Complutense of Madrid, 1992.
24 J. D. Jorgensen, B. Dabrowski, S. Pei, D. R. Richards and D. G. Hinks, *Phys. Rev. B*, 1989, **40**, 2187.
25 A. R. West, *Solid State Chemistry and its Applications*, Wiley, Chichester, 1984.
26 C. Chaillout, S. W. Cheong, Z. Fisk, M. S. Lehmann, M. Marezio, B. Morosin and J. E. Schriber, *Physica C*, 1989, **158**, 183.
27 C. Rial, E. Morán, M. A. Alario-Franco, U. Amador and N. H. Andersen, *Physica C*, 1995, **254**, 233.
28 M. H. Wangbo, M. Evain, M. A. Beno and J. M. Williams, *Inorg. Chem.*, 1987, **26**, 1829.
29 M. H. Wangbo, *Physica C*, 1989, **158**, 65.
30 T. Hahn, *International Tables for Crystallography*, Kluwer, Dordrecht, 1989, vol. A, 2nd edn.

Paper 6/05588E; *Received* 9th *August*, 1996