Superconducting (1:1:2:2)-type layered cuprates of the formula $TlCa_{1-x}L_xSr_2Cu_2O_y$ (L = Y or a rare-earth element)

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The $TlCa_{1-x}L_xSr_2Cu_2O_y$ (L=Y or a rare-earth element) series of cuprates possessing a (1:1:2:2)-type layered structure exhibit superconductivity in the 60–90-K region. The $TlL_xSr_2Cu_2O_y$ (x=1) series of cuprates also possess the (1:1:2:2)-type structure, but are not superconducting. A change in the conduction mechanism seems to occur in the $TlCa_{1-x}L_xSr_2Cu_2O_y$ system with a change in x. Partial substitution by Pb does not favor superconductivity in this series of cuprates.

Ever since the discovery of high-temperature superconductivity in thallium cuprates of the general formula $Tl_mCa_{n-1}Ba_2Cu_nO_{2n+2+m}$ (m=1 or 2),[1–7] we have been exploring the possibility of synthesizing other superconducting layered cuprates related to this family. In the $TlCa_{n-1}Ba_2Cu_nO_{2n+3}$ series, partial substitution of Ca by L (L=Y or a rare-earth element) does not favor superconductivity.[8] Partial substitution of Tl by Pb stabilizes $TlCa_{n-1}$- $Sr_2Cu_nO_{2n+3}$ and gives rise to high-T_c superconductivity. Accordingly, $Tl_{0.5}Pb_{0.5}CaSr_2Cu_2O_y$ and $Tl_{0.5}Pb_{0.5}Ca_2$- $Sr_2Cu_3O_y$ show superconducting transitions around 90 and 120 K, respectively.[9,10] We considered it most worthwhile to investigate the effect of substituting Ca^{2+} in $TlCaSr_2Cu_2O_7$ by a trivalent ion on the superconductivity. Towards this end we have carried out studies on several cuprates of the general formula $TlCa_{1-x}$-$L_xSr_2Cu_2O_y$. This study has revealed these cuprates to constitute a new series of high-T_c superconductors providing scope for examining several related series of cuprates with different cation substitutions and also to investigate changes in properties with composition as well as the rare earth.

Oxides of the formula $TlCa_{1-x}L_xSr_2Cu_2O_y$ were synthesized as follows. Initially a matrix of the component oxides other than Tl_2O_3 was prepared by heating $CaCO_3$, $SrCO_3$, L_2O_3 (except in the case of Pr and Tb where Pr_6O_{11} and Tb_4O_7 were used), and CuO at 1220 K for 24 h. The required quantity of Tl_2O_3 was mixed with the matrix, the mixture in the form of a thin pellet wrapped in a Pt foil and heated in a sealed silica ampoule at 1170 K for 2 h. The ampoule was then quenched to room temperature. The Pb-substituted samples were prepared in a similar fashion, with PbO being added along with Tl_2O_3 to the matrix before heating in a sealed ampoule. X-ray diffraction patterns of the powdered samples were carried out using a JEOL-8P diffractometer. Four-probe dc resistivity was measured on polycrystalline pellets. dc magnetic susceptibility measurements were carried out on powdered samples with a Faraday balance. X-ray photoelectron spectra were recorded with a VG Instrument spectrometer.

In Fig. 1 we show the powder x-ray diffraction patterns of a few members of the $TlCa_{1-x}L_xSr_2Cu_2O_y$ family along with those of the known superconductor of the (1:1:2:2)-type, $Tl_{0.5}Pb_{0.5}CaSr_2Cu_2O_y$. The figure clearly reveals the similarity in the patterns, which suggests that they all possess the 1:1:2:2 layered structure with two Cu-O sheets. We could accordingly index the patterns of the $TlCa_{1-x}L_xSr_2Cu_2O_y$ samples based on a primitive tetragonal cell with a c parameter of ~12 Å. We could obtain monophasic samples of several $TlCa_{0.5}L_{0.5}Sr_2$-

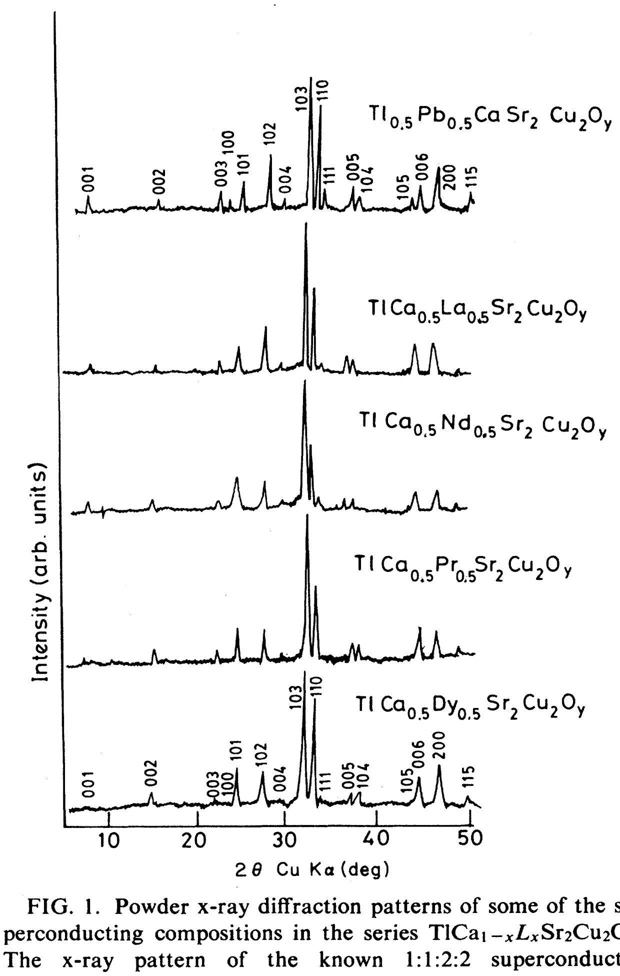

FIG. 1. Powder x-ray diffraction patterns of some of the superconducting compositions in the series $TlCa_{1-x}L_xSr_2Cu_2O_y$. The x-ray pattern of the known 1:1:2:2 superconductor $Tl_{0.5}Pb_{0.5}CaSr_2Cu_2O_y$ is shown for comparison.

Cu_2O_y members with different rare-earth ions as shown in Fig. 1. We have not yet been able to prepare the parent $TlCaSr_2Cu_2O_7$ in pure form, but the x-ray pattern of the impure sample leaves little doubt that it also has the 1:1:2:2 layered structure.

Unlike $TlCaSr_2Cu_2O_7$ which only shows indications of weak superconductivity around 50 K, $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$ compositions showed bulk superconductivity as can be seen from the typical magnetic susceptibility data given in Fig. 2; the percentage of the superconducting phase was ~30. The $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$ compositions by and large show sharp superconducting transitions as typified by the resistivity plots given in Fig. 3. The onset of superconductivity in these cuprates is generally in the 60–90 K range, the T_c decreasing with a decrease in the radius of the L^{3+} ion (Fig. 2). Substitution of Ca^{2+} by a L^{3+} ion seems to have the same effect as the substitution of Tl by Pb in $TlCaSr_2Cu_2O_7$. Accordingly, Pb L_{III} absorption edge spectra[11] show that Pb in $Tl_{0.5}Pb_{0.5}CaSr_2Cu_2O_y$ is in the 4+ state, thus making the total cationic charge (leaving out Cu) the same (+9.5) in this cuprate as in $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$. It is possible that the *L*-Tl-Sr-Ca-Cu-O system of superconductors reported by Sheng *et al.*[12] is the same as the (1:1:2:2)-type cuprates described here.

X-ray photoelectron spectra of $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$ in the Cu $2p_{3/2}$ region show a main feature around 932.5 eV and a broad, weaker feature (satellite) around 942 eV. The relative intensity of the satellite is a measure of the proportion of the Cu^{2+} $(3d^9)$ species in the ground state. We find that the ratio of the intensity of the satellite to that of the main peak is around 0.28 in $TlCa_{0.5}Pr_{0.5}Sr_2Cu_2O_y$ and 0.22 in $Tl_2CaBa_2Cu_2O_8$ (Fig. 4). In CuO, the ratio is 0.5. The nature of Cu states in the new series of Tl cuprates is also comparable to that in the recently discovered[13] $Pb_2Sr_2Ca_{1-x}L_xCu_3O_y$ family of superconductors which contain a considerable proportion of Cu^{1+} species.

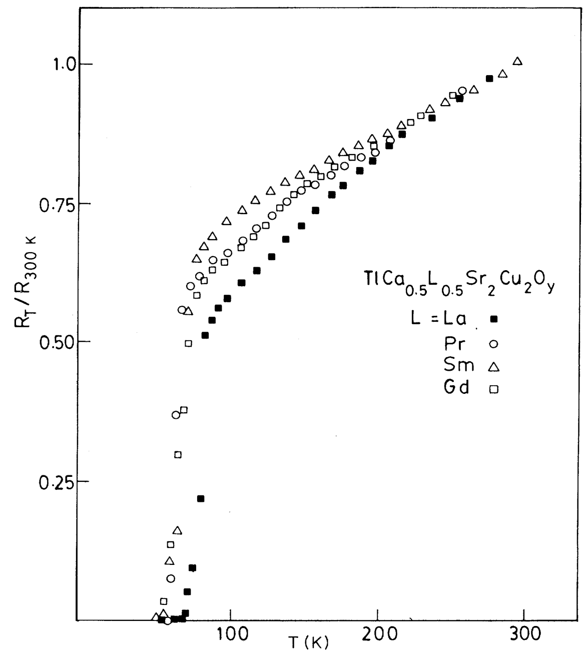

FIG. 3. Normalized resistivity plots of $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$.

We have prepared compounds of the type $TlLSr_2Cu_2O_y$ wherein the *L* ion completely replaces Ca^{2+} in $TlCaSr_2Cu_2O_7$. Members of the $TlLSr_2Cu_2O_7$ family also possess the 1:1:2:2 structure with two Cu-O sheets as evidenced from the x-ray diffraction patterns (Fig. 5), but they do not show superconductivity. It is not only necessary to have both Ca and *L* ions to obtain superconductivity in this system, but also a proper Ca to *L* ratio. Furthermore, a certain proportion of *L* (~20%) is essential to stabilize $TlCaSr_2Cu_2O_y$.

It is noteworthy that substitution of *L* in place of Ca in-

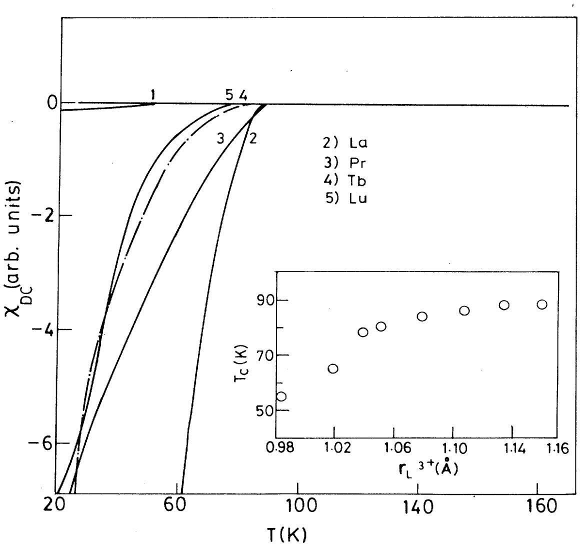

FIG. 2. dc magnetic susceptibility behavior of nominal $TlCaSr_2Cu_2O_y$ (1) and $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$ (2–5). Inset shows variation of T_c with the radius of L^{3+}.

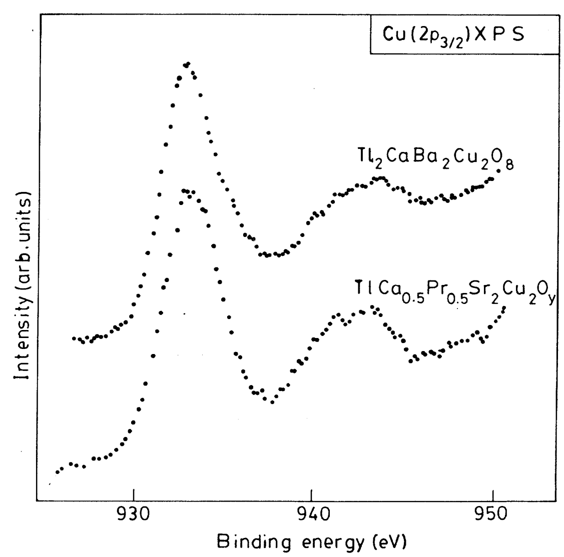

FIG. 4. X-ray photoelectron spectra of $TlCa_{0.5}Pr_{0.5}Sr_2Cu_2O_y$ and $Tl_2CaBa_2Cu_2O_8$ in the Cu ($2p_{3/2}$) region.

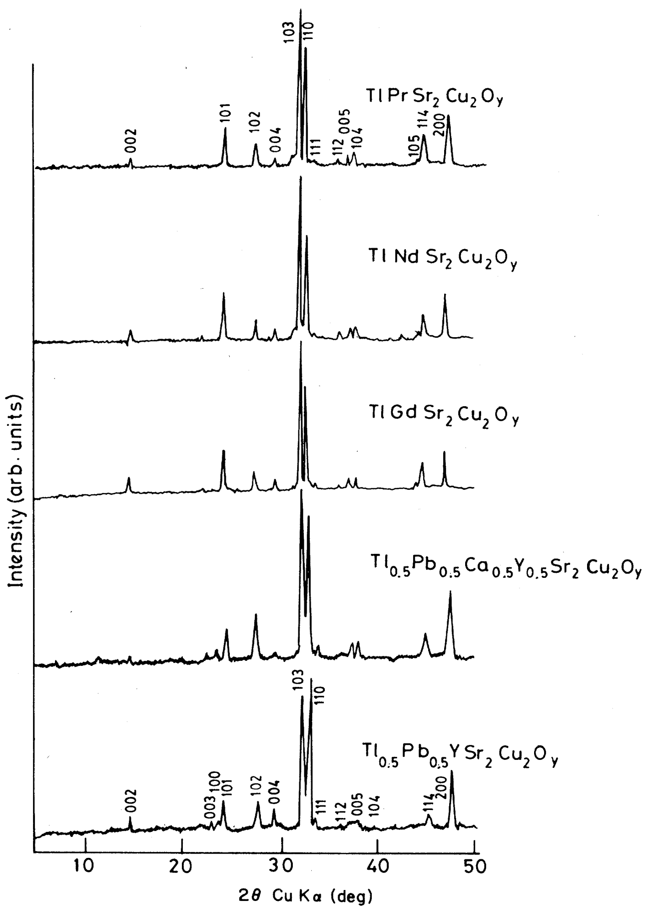

FIG. 5. Powder x-ray diffraction patterns of nonsuperconducting phases in the (Tl-Pb)-(Ca,L)-Sr-Cu-O system.

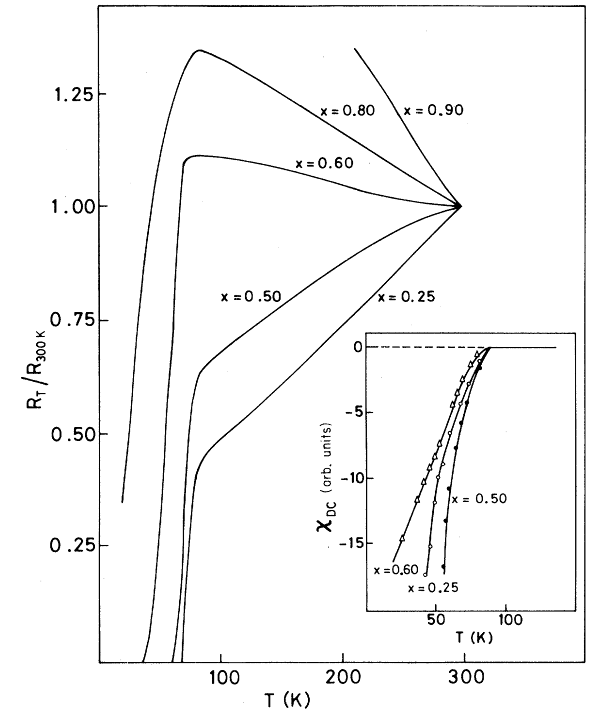

FIG. 6. Resistivity data of $TlCa_{1-x}Nd_xSr_2Cu_2O_y$. Note change from metallic to semiconducting behavior above $x = 0.5$. Inset shows dc susceptibility data indicating that T_c varies with x as $0.6 < 0.25 < 0.5$.

troduces electrons. Evolution of electronic properties in the $TlCa_{1-x}L_xSr_2Cu_2O_y$ series with increasing x is therefore of interest. Preliminary results (Fig. 6) show that beyond $d = 0.5$, the material is semiconducting in the normal state while it is metallic when $x \leq 0.5$. Assuming that the oxygen stoichiometry is not significantly affecting the trend, it seems possible that a hole mechanism changes to an electron mechanism at a critical value of x. Accordingly, the T_c value varies with x as $0.6 < 0.25 < 0.5$. The hole-electron balance in these materials is now being investigated in this laboratory. The variation of T_c with L in $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$ indicated earlier (Fig. 2) could be related to the nature of L-O bonding, with the larger ions being associated with higher ionicity.

We are able to substitute Tl in $TlCa_{0.5}L_{0.5}Sr_2Cu_2O_y$ partly by Pb. The x-ray pattern of monophasic $Tl_{0.5}Pb_{0.5}Ca_{0.5}Y_{0.5}Sr_2Cu_2O_y$ with the 1:1:2:2 structure is shown in Fig. 5, but it is a semiconductor. We similarly find that $Tl_{0.5}Pb_{0.5}YSr_2Cu_2O_y$ possessing the 1:1:2:2 structure (Fig. 5) is not superconducting. Accordingly, the ratio of the intensities of the satellite and the main feature in the Cu $2p_{3/2}$ spectra of the semiconducting $Tl_{0.5}Pb_{0.5}Ca_{0.5}Y_{0.5}Sr_2Cu_2O_y$ and $Tl_{0.5}Pb_{0.5}YSr_2Cu_2O_y$ is between 0.4 and 0.5. We are continuing to investigate several members related to the Tl(Pb)-Ca(L)-Sr-Cu-O system.

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