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The Occurrence of Superconductivity in the $TlBa_2CuO_{5-\delta}$-Type (1021) System

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Stable and reproducible superconductivity in the $Tl(Ba_{2-x}La_x)CuO_{5-\delta}$ $(0.0 \le x \le 0.6)$ system with the tetragonal $TlBa_2CuO_{5-\delta}$-type (1021) structure was reported. A Prototype compound $TlBa_2CuO_{5-\delta}$ had shown a metastable superconducting onset around 25 K, with zero resistivity at 10 K. With partial substitution of La for Ba ions, T_c (50% resistivity drop) increases to 45 K, T_{c0} (zero resistivity) to 42 K and onset around 50 K. A diamagnetic signal was observed with onset as high as 57 K. Tetragonal lattice parameters decrease with the increasing La concentration due to the partial replacement of larger Ba^{2+} ions by smaller La^{3+} ions. The Pairing field energy of 170 K and electron-elementary excitation coupling constant λ of 0.76 were derived from the BCS-like T_c formula through comparison with other single Tl–O layer systems $TlCa_{n-1}Ba_2Cu_nO_{2n+3-\delta}$.

KEYWORDS: $TlBa_2CuO_5$-type (1021) superconductor, metal-insulator transition

Recently, seven superconducting phases were synthesized in the Tl–Ca–Ba–Cu oxide system $Tl_mCa_{n-1}Ba_2Cu_nO_{m+2n+2}$ ($m=1$, 2 and $n=1$, 2, 3, 4), with the superconducting transition temperature $T_c=0$–80 K for (2021), 95–110 K for (2122), 120–125 K for (2223), 105–120 K for (2324), 65–85 K for (1122), 100–110 K for (1223) and 120–122 K for (1324).[1-16] However, no superconductivity down to 4.2 K was reported in the Ca-free $TlBa_2CuO_5$ (1021) compound.[11,13] This is quite puzzling, since all other systems with the CuO_6 octahedron show superconductivity. For the $(La_{2-x}Ba_x)CuO_4$ system,[17,18] T_c varied from nonsuperconducting for $x<0.05$ to a maximum T_c value of 35 K at $x=0.15$. For the compound $Bi_2Sr_2CuO_6$ (2021),[19,20] T_c ranges from 0–22 K were reported. For the compound $Tl_2Ba_2CuO_6$ (2021),[1,12,13] T_c ranges from 0–80 K were reported. Comparing the variation of T_c and the metal-insulator transition in these oxide superconductors, it appears that the $TlBa_2CuO_5$ compound is near the metal-insulator transition boundary. We believe that using careful sample preparation conditions and/or suitable substitution, superconductivity can be stabilized and enhanced. Here we report stable and reproducible superconductivity in the $Tl(Ba_{2-x}La_x)CuO_{5-\delta}$ system $(0.0 \le x \le 0.6)$ with the tetragonal $TlBa_2CuO_{5-\delta}$-type (1021) structure.

Samples were synthesized by the solid-state reaction method. High-purity powders of the Tl_2O_3 and $(Ba_{2-x}La_x)CuO_{3+\delta}$ $(0.0 \le x \le 0.6)$ precursor were well mixed, ground and then pressed into pellets. These pellets were wrapped in gold foils and individualy placed in a gold-foil-covered alumina crucible, reacted in flowing oxygen at 895°C ($x=0.0$) or 910°C ($x=0.2$, 0.4 and 0.6) for 10 minutes, annealed at 880°C for 4 hours and then cooled to room temperature at a rate of 1°C/min. AC electrical resistivity measurements (16 Hz) were carried out using a standard four-probe method with silver paint contact, and the samples were cooled in a Cryosystems LTS-21 closed-cycle refrigerator from 300 K to 8 K. Low-field magnetization data were obtained by using a PAR 155 vibrating-sample magnetometer (VSM) from 5 K to 100 K. Powder X-ray diffraction data were obtained from a Shimadzu XD-3 diffractometer equipped with a diffracted beam crystal monochromator.

The temperature dependence of the electrical resistivity for the prototype compound $TlBa_2CuO_{5-\delta}$ (1021) is shown in Fig. 1. This sample was prepared at 895°C since it melted at 910°C. Metallic behavior was observed with relatively large room temperature resistivity of ρ(300 K) $=36$ mΩ cm. Metastable superconducting transition occurred with an onset around 25 K and zero resistivity T_{c0} at 10 K. Meissner signal (field-cooled in 100 G) showed T_c onset around 15 K and mass diamagnetic susceptibility

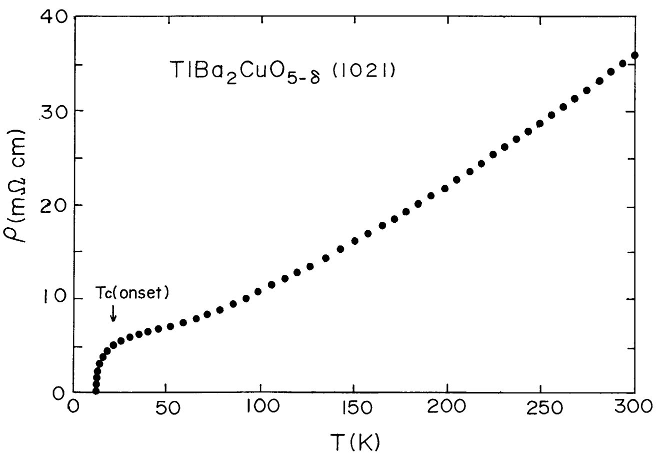

Fig. 1. Temperature dependence of electrical resistivity for the prototype compound $TlBa_2CuO_{5-\delta}$ (1021). Metastable superconducting onset around 25 K and zero resistivity T_{c0} around 10 K were observed.

$\chi_g = -1.7\times10^{-4}$ cm^3/g at 5 K (Fig. 2). Here the powder X-ray diffraction result shows almost single-phase tetragonal patterns with lattice parameters $a=3.859(4)$ Å, $c=9.229(9)$ Å with small amounts of unreacted Ba_2CuO_3 precursors. No $Tl_2Ba_2CuO_{6-\delta}$-type phase (2021) can be detected. Large room temperature electrical resistivity, low-T_c, a low fractional Meissner signal and good single-phase X-ray patterns indicate that the metallic compound $TlBa_2CuO_5$ is very near the metal-insulator transition boundary.

The superconducting transition temperature T_c of this (1021) tetragonal phase can be dramatically enhanced through partial substitution of Ba^{2+} ions by smaller La^{3+} ions. The temperature dependence of the electrical resistivity for the $Tl(Ba_{2-x}La_x)CuO_{5-\delta}$ system prepared at 910°C ($x=0.2$, 0.4 and 0.6) is shown in Fig. 3. Room temperature electrical resistivity decreases rapidly from 36 mΩ cm for $x=0.0$, to 14 mΩ cm for $x=0.2$, 2.1 mΩ cm for $x=0.4$ and 1.4 mΩ cm for $x=0.6$. The superconducting transition temperature T_c (50% resistivity drop from linear resistivity deviation) increases sharply from 15 K for $x=0.0$, to 42 K for $x=0.2$, 40 K for $x=0.4$ and 45 K for $x=0.6$. The highest T_{c0} is observed at 42 K for $x=0.6$. A small resistivity deviation with onset around 57 K for $x=0.2$ is also obtained from a diamagnetic signal, as shown in Fig. 2. Mass diamagnetic susceptibility χ_g (100 G field-cooled) of -8×10^{-4} cm^3/g at 5 K is observed for both $x=0.2$ and 0.6. This value is nearly five times the value for the prototype compound $TlBa_2CuO_5$ even with the small grain size of about 1 μm, as observed from SEM studies, due to the short reaction period.[15]

The powder X-ray diffraction patterns for the $Tl(Ba_{1.4}La_{0.6})CuO_{5-\delta}$ sample are shown in Fig. 4. All lines can be indexed with the tetragonal $TlBa_2CuO_5$-type phase except for small amounts of unreacted Ba_2CuO_3. No $(La_{1.85}Ba_{0.15})CuO_4$ ($T_c\leq35$ K), $Tl_2Ba_2CuO_6$ or $LaBa_2Cu_3O_7$-type phases can be detected from the diffraction patterns under the present sample preparation conditions. Tetragonal (1021) phase lattice parameters a and c, and unit cell volume V were obtained using a scanning rate of 0.25° in 2θ per minute with a Si standard to eliminate any systematic errors. Relative line intensities could be fitted nicely using the space group P4/mmm[12] and program LAZY PULVERIX-PC.[21] Lattice parameters decreased with the increasing La concentration due to the partial replacement of the larger Ba^{2+} ions by smaller La^{3+} ions.

Similar superconductivity stabilization and enhancement for the CuO_6-octahedron system $Bi_2(Sr_{2-x}La_x)CuO_{6-\delta}$ ($0.0\leq x\leq1.0$) were also observed. With partial substitution of La for Sr, superconductivity increased from below 6 K for the prototype compound $Bi_2Sr_2CuO_{6-\delta}$ to $T_c=27$ K for the $Bi_2(Sr_{1.5}La_{0.5})CuO_{6-\delta}$ compound, with a T_{c0} of 19 K and T_c onset up to 35 K.[22] The stabilization and enhancement of superconductivity for these two systems can be attributed to the different valency between La^{3+} ions and A^{2+} (A=Ba, Sr) ions, which play the role of electron donors and thus move the compounds away from the metal-insulator transition boundary into a stable superconducting region.

Comparing the maximum T_c of 45 K in the (1021) phase with other single Tl-O layer systems,

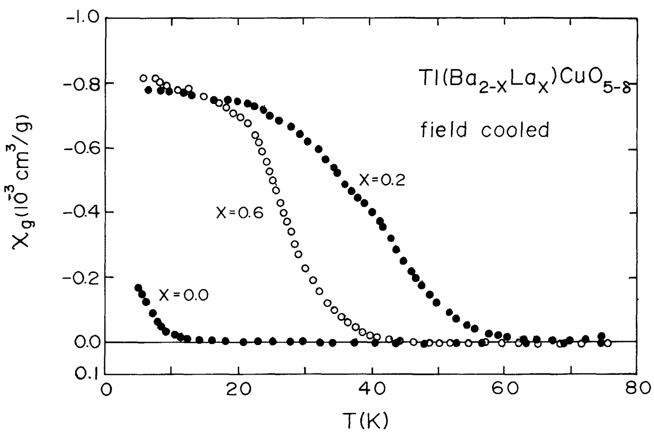

Fig. 2. Temperature dependence of mass diamagnetic susceptibility χ_g (field-cooled in 100 G) for the system $Tl(Ba_{2-x}La_x)CuO_{5-\delta}$ ($x=0.0$, 0.2 and 0.6).

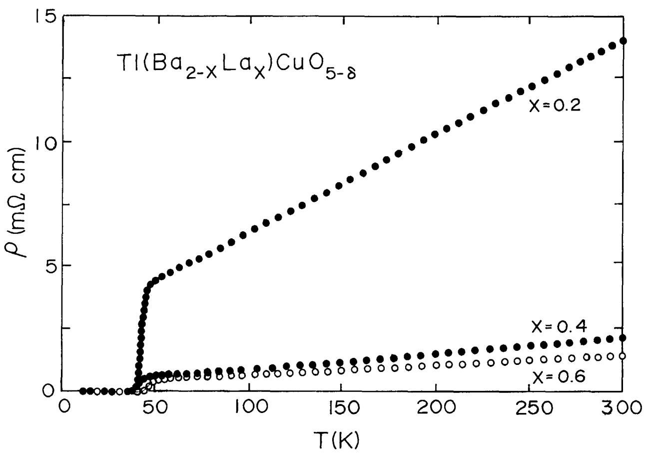

Fig. 3. Temperature dependence of electrical resistivity for the system $Tl(Ba_{2-x}La_x)CuO_{5-\delta}$ ($x=0.2$, 0.4 and 0.6).

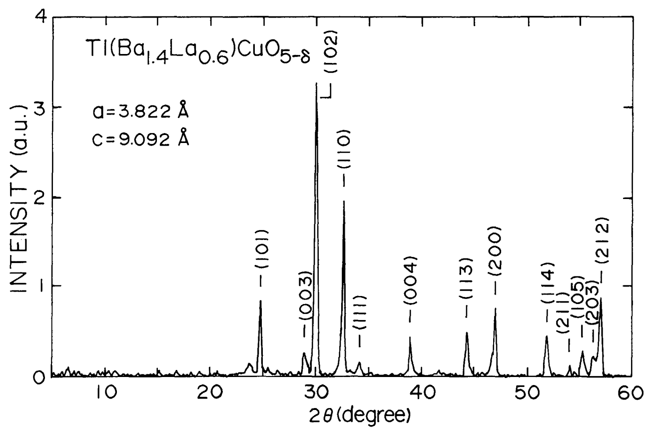

Fig. 4. Powder X-ray diffraction patterns for the $Tl(Ba_{1.4}La_{0.6})CuO_{5-\delta}$ sample. The patterns can be indexed with the tetragonal $TlBa_2CuO_{5-\delta}$-type (1021) structure with $a=3.822$ Å and $c=9.092$ Å.

$TlCa_{n-1}Ba_2Cu_nO_{2n+3-\delta}$; i.e. the 85 K (1122) phase, 110 K (1223) phase and 122 K (1324) phase, these values can be nicely fitted using the BCS-like formula $k_BT_c=\hbar\omega_c$

$\exp(-1/\lambda n)$, where n is the number of Cu Layers, k_B is the Boltzmann constant and $\hbar$ is Planck's constant $h/2\pi$. A pairing field energy $\hbar\omega_c/k_B$ of 170 K with an electron-elementary excitation coupling constant λ of 0.76 were derived. For the two Tl–O layers systems $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4+\delta}$ ($n=1$, 2, 3), a smaller pairing field energy of 150 K and larger coupling constant of $\lambda=1.53$ were obtained. For $n=4$ (2324),[16] it is still not clear whether the lower T_c of 120 K is due to the difficulty of sample preparation or other factors.

In conclusion, metastable superconductivity with zero resistivity around 10 K was observed in the prototype compound, $TlBa_2CuO_{5-\delta}$. Superconductivity of this (1021)-type phase was stabilized and enhanced with partial substitution of Ba^{2+} ions by La^{3+} ions, where the transition temperature T_c as high as 45 K and onset around 57 K were observed.

Acknowledgements

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