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Superconductivity above 77 K in the *R*-Tl-Sr-Ca-Cu-O system (*R* represents rare earths)

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Superconductivity at 80–90 K has been resistively and magnetically observed in the *R*-Tl-Sr-Ca-Cu-O systems (*R* represents the rare earths including Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu and excepting Ce) in which five metal elements all are required for the superconductivity. In particular, the Pr-Tl-Sr-Ca-Cu-O system and Tb-Tl-Sr-Ca-Cu-O system are the first superconducting systems above 77 K in which Pr or Tb are required for the superconductivity. We believe that even higher critical temperatures may be achieved by optimizing the starting composition and preparation conditions, and/or by further elemental substitutions.

Discoveries of the Tl-based superconducting systems[1–3] have provided increased T_c, with zero-resistance temperatures as high as 125 K.[4–7] A number of Tl-based superconducting compounds have been identified, including the series $Tl_mBa_2Ca_{n-1}Cu_nO_{1.5m+2n+1}$ with $m=2$ (Refs. 6–11) and 1,[12,13] and $n=1$–4.[6–13] The T_c of these compounds increases with n as well as m. These trends have stimulated a strong search for higher T_c Tl-based superconductors by increasing n and/or m. On the other hand, search for new and even higher temperature Tl-based superconducting systems has been also widely carried out. In extensive elemental substitutions, we have observed superconductivity at 20 and 70 K in the Tl-Sr-Ca-Cu-O system.[14] Although a sharp drop in resistance at about 100 K was observed in our early experiments and a similar superconductivity was reported by other groups,[15,16] these results are difficult to reproduce, suggesting that the formation of this high-temperature superconducting phase is very sensitive to preparation procedure. Recently, Subramanian *et al.*[17] found that addition of Pb into Tl-Sr-Ca-Cu-O system results in formation of high temperature Tl-Pb-Sr-Ca-Cu-O superconducting phases. Two phases, with T_c 80–90 K for $(Tl_{0.5}Pb_{0.5})Sr_2CaCu_2O_7$ and 120 K for $(Tl_{0.5}Pb_{0.5})$-$Sr_2Ca_2Cu_3O_9$, have been identified. We have obtained similar results.[18] In this paper, we report superconductivity at 80–90 K in the *R*-Tl-Sr-Ca-Cu-oxide systems with *R* representing the rare earths including Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu and excepting Ce. In these systems, five metal elements all are required for the 80–90 K superconductivity. In particular, the Pr-Tl-Sr-Ca-Cu-O system and Tb-Tl-Sr-Ca-Cu-O system are the first superconducting systems above 77 K in which Pr or Tb are required for the superconductivity. We believe that higher T_C may be achieved by optimizing starting composition and preparation conditions. We also believe that new, even higher temperature superconducting systems may be discovered by further elemental substitutions for these systems.

The *R*-Tl-Sr-Ca-Cu-oxide samples were prepared using high-purity Tl_2O_3, $SrCO_3$, $CaCO_3$, CuO, and rare-earth oxides (R_2O_3 with exceptions of CeO_2 and Tb_4O_7). First, appropriate amounts of $SrCO_3$, $CaCO_3$, and CuO were mixed and ground. The mixture was heated at 950 °C in air for at least 24 h with several intermediate grindings. The resulting Sr-Ca-Cu-O powder served as master material. In a typical procedure, appropriate amounts of Sr-Ca-Cu-O powder, Tl_2O_3, and a rare-earth oxide were mixed, ground, and pressed into a pellet with a diameter of 7 mm and a thickness of 1–2 mm. The pellet was put into a furnace, which had been heated to 900 °C, and was heated in flowing oxygen for 5 min, followed by furnace cooling. Both low-frequency ac resistance and dc resistance were measured by the standard four-probe technique with silver-paste contact. Low-frequency (5-kHz) ac susceptibility was measured using the technique of Norton.[19]

Figure 1 shows ac resistance versus temperature curves down to 77 K for samples whose starting compositions were given by $RTl_2Sr_2Ca_2Cu_3O_{11.5}$ (hereafter, *R* 1:2:2:2:3), where *R* represents the rare earths Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. All samples except *R* = Ce showed a sharp drop in resistance in the range of 80–90 K. Resistance temperature variations in the normal state were linear for most sam-

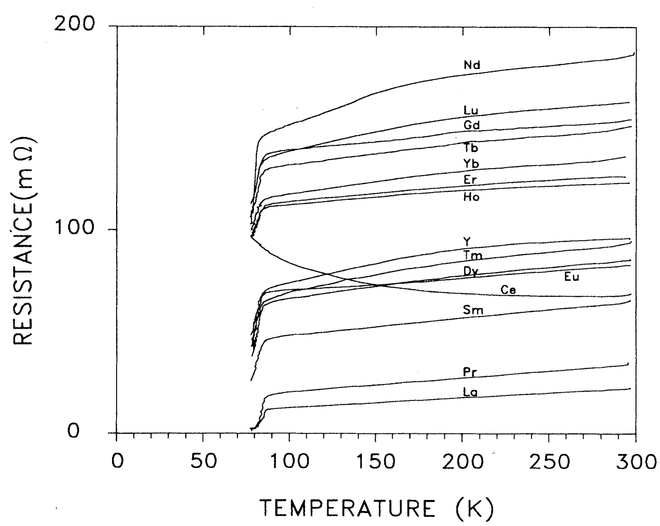

FIG. 1. Temperature dependences of the ac resistance for *R* 1:2:2:2:3 samples prepared using the typical procedure.

ples. Some samples (e.g., Y, Nd, and Lu) showed a deviation from linearity at much higher temperatures. Superconducting behavior of the *R*-Tl-Sr-Ca-Cu-O samples is sensitive to both starting composition and preparation conditions. Figure 2 shows dc resistance versus temperature curves down to 77 K for some *R*-Tl-Sr-Ca-Cu-O samples with different starting compositions prepared under the different conditions specified in the caption. Note that samples Pr2, Pr3, and La1 reach zero resistance at 77 K. Figure 3 shows dc resistance versus temperature curves down to 15 K for two Tb-containing samples (Tb3 and Tb4) and one Yb-containing sample (Yb1), as examples for those samples which do not reach zero resistance at 77 K. The onset temperatures of these samples are about the same (91 K), and zero-resistance temperatures are 45 K for Tb3, 69 K for Tb4, and 72 K for Yb1. We believe that the superconducting behavior of *R*-Tl-Sr-Ca-Cu-O samples can be improved by optimizing starting composition and preparation conditions.

Low-frequency ac susceptibility measurements on *R*-Tl-Sr-Ca-Cu-O samples showed similar superconducting transitions. Figure 4 shows ac susceptibility versus temperature curves for a Pr 1:2:2:2:3 sample and a Tb 1:2:2:2:3 sample. Comparing with high-quality Tl-Ba-Ca-Cu-O superconducting samples about 5% volume of material was superconducting at 77 K for the Pr 1:2:2:2:3 sample, and about 1% for the Tb 1:2:2:2:3 sample. Note that this estimation is semiquantitative because we have assumed that ac susceptibility at 77 K represents the same fraction of superconducting material at the same temperature for both Tl-Ba-Ca-Cu-O samples and *R*-Tl-Sr-Ca-Cu-O samples. Also note that from the shape of ac susceptibility-temperature curves shown in Fig. 4, the

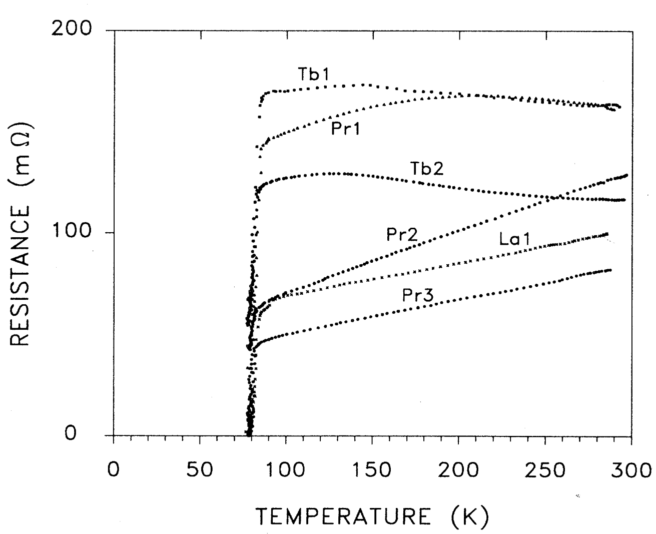

FIG. 2. Temperature dependences of the dc resistance for some *R*-Tl-Sr-Ca-Cu-O samples with different starting compositions and prepared under different conditions: Tb1, Tb 1:1:2:4:5, 950 °C, 3 min, quenching; Tb2, Tb 1:1:2:4:5, 900 °C, 3 min, annealing (710 °C, 10 h); Pr1, Pr 1:1:2:4:5, 950 °C, annealing (710 °C, 10 h); Pr2, Pr 1:2:2:2:3, 950 °C, 2 min, furnace cooling; Pr3, Pr 1:2:2:2:3 , 900 °C, 5 min, furnace cooling; La1, La 1:2:2:2:3, 900 °C, 5 min, furnace cooling.

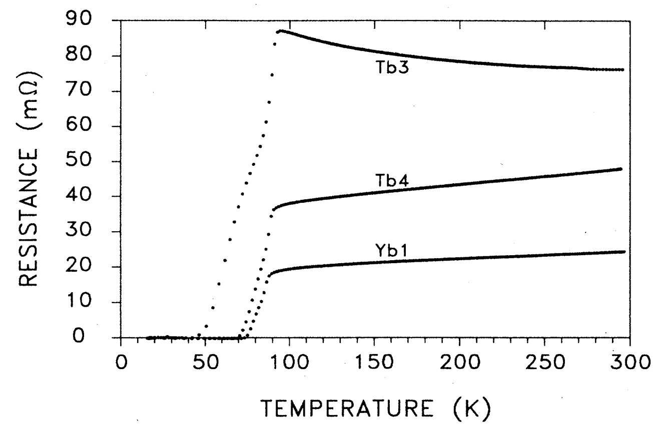

FIG. 3. Temperature dependences of dc resistance down to 15 K for two Tb-containing samples and one Yb-containing sample. Tb3, Tb 1:2:2:2:3, 875 °C, 4 h, furnace cooling. Tb4, Tb 1:2:2:2:3, 950 °C, 3 min, quenching. Yb1, Yb 1:2:2:2:3, 950 °C, 3 min, quenching.

fraction of superconducting material in *R*-Tl-Sr-Ca-Cu-O samples at lower temperature must be much greater than that at 77 K.

Since superconductivity above 77 K has been reported both in the Tl-Sr-Ca-Cu-O system[14–16] and in the Y-Sr-Cu-O system,[20] we carried out a series of systematic experiments removing each component from the *R*-Tl-Sr-Ca-Cu-O system. The results showed that using our experimental conditions, removal of any element resulted in the disappearance of superconductivity above 77 K, suggesting that all the five metal elements are required for the observed 80–90 K superconductivity. It is noteworthy that one of the most important results in the present experiment is the observation of superconductivity above 77 K in the Pr- and Tb-containing samples in which Pr or Tb

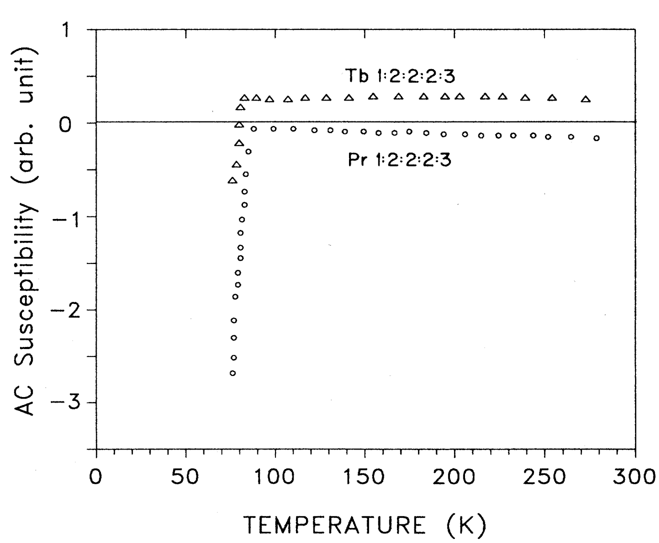

FIG. 4. ac susceptibility vs temperature curves for a Pr 1:2:2:2:3 sample and for a Tb 1:2:2:2:3 sample.

are required for the superconductivity. As of this writing, Ce is the only rare earth which has not been observed to produce an above 77-K superconductivity in any oxide system in which Ce exists as a required component for superconductivity.

The compositional and structural determinations of the *R*-Tl-Sr-Ca-Cu-O superconducting phase are in progress. Preliminary x-ray powder diffraction for a Pr 1:2:2:2:3 sample showed a pattern similar to that of 1:2:1:2: phase of lead-substituted Tl-Sr-Ca-Cu-O.[17] A 1:2:2:3 phase with higher T_c is expected, although superconductivity from such a phase has not been unambiguously observed. At any rate, the *R*-Tl-Sr-Ca-Cu-O system would not form only one superconducting phase. In fact, the resistance versus temperature curve of the sample Tb3 in Fig. 3 has clearly showed two superconducting onsets: one at 91 K and the other at about 70 K. Furthermore, if the rare earth exists as an independent component in a *R*-Tl-Sr-Ca-Cu-O superconducting phase, i.e., a new superconducting phase has formed, higher-T_c superconducting systems may be discovered by further elemental substitutions for these systems. In particular, there seems to be a trend that the highest T_c which a superconducting system can reach may increase with complexity of this system: two-metal system reaches 30 K (La-Cu-O); three-metal system reaches 90 K (*R*-Ba-Cu-O); four-metal system reaches 125 K (Tl-Ba-Ca-Cu-O). One might expect that the five-metal *R*-Tl-Sr-Ca-Cu-O superconducting system may lead to superconductivity with T_c much higher than 125 K, the highest T_c reported so far.

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