Semiconducting TlSr$_2$RCu$_2$O$_7$ (R = rare earth) and its superconducting derivatives


Department of Physics, University of Arkansas, 105 Physics Building, Fayetteville, AR 72701, USA

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Semiconducting TlSr$_2$RCu$_2$O$_7$ (R = Pr or Er) with a 1212-type structure has been synthesized in the single-phase form. Partial substitution of Sr$^{2+}$ for R$^{3+}$ converts this semiconductor to a 90 K superconductor TlSr$_2$(R$_{1-y}$Sr$_y$)Cu$_2$O$_7$. A combination substitution, Sr$^{2+}$ for R$^{3+}$ and Pb$^{4+}$ for Tl$^{3+}$, leads to the Ca-free 100 K superconductor (Tl, Pb)Sr$_2$(R, Sr)Cu$_2$O$_7$. The results are explained in the framework of the mixed Cu$^{2+}$/Cu$^{3+}$ valence.

1. Introduction

The discoveries of the 90 K TlBaCuO and 120 K TlBa-CaCuO systems [1-4] have led to a number of new Tl-based superconducting systems. Among them is the TlSrCaCuO system [5]. When a rare earth (R) is introduced into this system, the TlSrCaCuO system exhibits superconductivity at about 90 K [6]. The phase responsible for the superconductivity is TlSr$_2$(Ca, R)Cu$_2$O$_7$ (1212 phase) [7]. Meanwhile, other 1212-type Tl-based superconductors (Tl, M)Sr$_2$CaCu$_2$O$_7$ and (Tl, M)Sr$_2$(Ca, R)Cu$_2$O$_7$ with M = Pb or/and Bi were also reported [8-11]. Further work showed that when R is added to the TlSrCuO system, the Ca-free TlSrCuO system is superconducting up to about 90 K [12, 13], and the phase responsible for the 90 K superconductivity is also a 1212-type compound TlSr$_2$(Sr, R)Cu$_2$O$_7$ [13]. From the point of view of the R-substitution, therefore, the compound TlSr$_2$SrCu$_2$O$_7$ would be synthesized. After many efforts, however, we were unable to prepare the 1212-type compound TlSr$_2$SrCu$_2$O$_7$, instead, we did successfully synthesize single phase 1212-type TlSr$_2$R$_x$Cu$_2$O$_7$ which is a semiconductor. It turned out that Sr-substitution for R in the semiconducting TlSr$_2$R$_x$Cu$_2$O$_7$ produced the 90 K superconducting TlSr$_2$(R, Sr)Cu$_2$O$_7$. In this paper, we report the synthesis and identification of the semiconductor TlSr$_2$RCu$_2$O$_7$ (R = Pr or Er). We give its superconducting derivatives TlSr$_2$(R$_{1-y}$Sr$_y$)Cu$_2$O$_7$ and (Tl$_{1-x}$Pb$_x$)Sr$_2$(R$_{1-y}$Sr$_y$)Cu$_2$O$_7$. The latter is the first Ca-free superconductor with $T_c$ above 100 K [14, 15]. The results are discussed in terms of the concept of the mixed Cu valence.

2. Experimental

The samples were prepared using high-purity oxides Tl$_2$O$_3$, SrO, Pr$_6$O$_{11}$, Er$_2$O$_3$, and CuO. In a typical procedure, component oxides with a certain metallic atom ratio were completely mixed and ground. The powder was pressed into a pellet with a diameter of 15 mm and a thickness of about 2 mm under a pressure of 7,000 kg/cm$^2$. The pellet was placed in an alumina tube. The opening of the tube was covered with an alumina plug. The alumina tube with contents was then put into a preheated tube furnace, and heated at about 1000 °C in flowing oxygen for 30 min., followed by furnace cooling to below 200 °C. Note that in the present experiments, Tl in starting compositions is in excess by 20% over the 1212 stoichiometry in order to compensate the Tl loss during heating. The resultant samples were examined by resistance measurements and by powder x-ray diffraction analyses. Resistance (ac, 27 Hz) was measured by the standard four-probe technique with silver paste contacts. All measurements were made with computer control and processing and were carried out in a commercial APD closed cycle refrigerator. Powder x-ray diffraction was carried out with Cu-K$\alpha$ radiation with use of a DIANO DIM 1057 diffractometer.

3. Results

Single phase sample was synthesized for both TlSr$_2$PrCu$_2$O$_7$ and TlSr$_2$ErCu$_2$O$_7$. The powder x-ray diffraction pattern for TlSr$_2$PrCu$_2$O$_7$ could be indexed based on a tetragonal structure with unit cell of $a = 3.845(1)$ Å and $c = 12.098(2)$ Å. Similarly, the diffraction pattern for TlSr$_2$ErCu$_2$O$_7$ could be indexed as a tetragonal unit cell of $a = 3.804(1)$ Å and $c = 11.993(2)$ Å.
Figure 1 shows the diffraction pattern for TlSr$_2$ErCu$_2$O$_7$ as an example. The structure of the 1212 phase TlSr$_2$RCu$_2$O$_7$ is very similar to that of the 123 phase RBa$_2$Cu$_3$O$_{7-δ}$. The only difference is that the Cu–O chain in the 123 structure is replaced by the Ti–O plane in the 1212-type structure (and Ba by Sr).

The R in TlSr$_2$RCu$_2$O$_7$ can be substituted partially by Sr, while the 1212 structure remains unchanged. In a series of samples TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$ with $y = 0.0$–1.0, the samples with $y = 0.0$–0.5 were essentially pure 1212 phase. When $y > 0.5$, an orthorhombic 1201 phase [13] appeared, and increased with $y$. When $y = 1.0$, the sample became nearly pure 1201 phase. Serial samples TlSr$_2$(Er$_{1-y}$Sr$_y$)Cu$_2$O$_7$ showed similar results. Figure 2 shows a plot of lattice parameters $a$ and $c$ as a function of $y$ for TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$ and TlSr$_2$(Er$_{1-y}$Sr$_y$)Cu$_2$O$_7$ with $y = 0.0$–0.5. The lattice parameters for TlSr$_2$(Er$_{1-y}$Sr$_y$)Cu$_2$O$_7$ are smaller than those of TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$. This is due to the size effect of metallic ions since Er$^{3+}$ has an ionic radius smaller than that of Pr$^{3+}$ (the effective ionic radius for 8-fold coordination is 1.004 Å for Er$^{3+}$, 1.126 Å for Pr$^{3+}$, and 1.26 Å for Sr$^{2+}$ [16]). The $c$-axes for both TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$ and TlSr$_2$(Er$_{1-y}$Sr$_y$)Cu$_2$O$_7$ increase with $y$. This is also a reflection of the size effect; substitution of larger Sr$^{2+}$ for smaller R$^{3+}$ results in the increase of the $c$-axes. The $a$-axis for TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$ decreases with $y$, whereas the $a$-axis of TlSr$_2$(Er$_{1-y}$Sr$_y$)Cu$_2$O$_7$ does not show such a variation fashion. These results can not be explained simply by the size effect, and will be discussed later.

Resistance measurements indicated that TlSr$_2$RCu$_2$O$_7$ (R = Pr or Er) prepared using the typical procedure is a semiconductor. When R is substituted partially by Sr, the samples TlSr$_2$(R, Sr)Cu$_2$O$_7$ became superconducting. Figure 3 shows resistance-temperature curves for samples TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$ with $y = 0.0$–0.5 which are nearly pure 1212 phase. It can be seen that the sample of $y = 0.0$ (i.e., TlSr$_2$PrCu$_2$O$_7$) is a semiconductor. With the increase of $y$, the samples become superconducting at $y = 0.1$–0.2. The samples of $y = 0.4$–0.5 exhibit the best superconducting behavior with zero-resistance temperatures up to 83 K. Note that the room-temperature resistivity of the samples TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$ decreased by a factor of $> 1000$ when $y$ increased from 0.0 to 0.5. When $y > 0.5$, the room-temperature resistivity of the samples remained low, but their superconducting behavior was gradually depressed. Figure 4 shows resistance-temperature curves for the samples TlSr$_2$(Pr$_{1-y}$Sr$_y$)Cu$_2$O$_7$ with $y = 0.6$–1.0. The sample of $y = 1.0$ (nearly pure 1201 phase) is metallic, but is not superconducting down to 15 K. It is interesting to point out that the temperature at the transition midpoint of the samples for 0.6–0.9 remained unchanged, suggesting that the 1212 phase in these samples may have a constant